

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
27 September 2001 (27.09.2001)

PCT

(10) International Publication Number
WO 01/70859 A2

- (51) International Patent Classification⁷: C08J 9/00 F-67540 Ostwald (FR). PARK, Chung, P. [US/DE]; Schulstrasse 10a, 76532 Baden-Baden (DE).
- (21) International Application Number: PCT/US01/04594
- (22) International Filing Date: 13 February 2001 (13.02.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 60/190,717 17 March 2000 (17.03.2000) US
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- (81) Designated States (national): AU, BR, CA, CN, CZ, HU, IL, IN, JP, KR, MX, NO, RU, US, ZA.
- (84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).
- Published:
— without international search report and to be republished upon receipt of that report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/70859 A2

(54) Title: PREPARATION OF A MACROCELLULAR ACOUSTIC FOAM

(57) Abstract: A process for making a macrocellular acoustic foam is disclosed in which a foamable gel comprising a blowing agent and a polymeric resin composition is subjected to an extrusion process characterized by a die pressure greater than the prefoaming critical die pressure but less than or equal to four times that of said prefoaming critical die pressure and macrocellular foams are disclosed obtainable by that process which are made of: A) one or more homopolymers of ethylene, one or more C₃-C₂₀ α-olefin polymers, or a combination thereof; B) one or more halogenated flame retardants; C) optionally, one or more polymers other than that of Component A; and D) optionally, one or more flame retardant synergists.

PREPARATION OF A MACROCELLULAR ACOUSTIC FOAM

BACKGROUND OF THE INVENTION

5 Foams and foamed articles often find utility in acoustic systems for sound absorption and insulation. Such foams, when developed for different market segments (appliance, automotive, building & construction, etc) often need to meet certain acoustic performance requirements and applicable fire test codes. To achieve the desired fire rating, a variety of flame retardants are often added to such foam resin formulations. Unfortunately, the typical flame retardants and other additives added to the formulation cause a number of foam problems. Flame retardants cause poor cell structure and cell collapse due to their effects on the polymer gel viscosity and melt strength. Flame retardants also act as nucleating agents in the foaming process and provide additional nucleation sites, resulting in the formation of a large number of small cells with variable properties. Unfortunately, small cell foam is not as acoustically active as large cell foam for sound absorption.

15 US Patent No. 4,277,569 teaches the preparation of flame retardant polyolefin foams for thermal insulation and padding. However, the patent does not describe macrocellular foams or flame retardant macrocellular foams for acoustic applications or their preparation.

Copending U.S. Application No. 60/178,516 filed on January 19, 2000 in the name of Martin Reimers et al., teaches the composition of macrocellular foams useful in sound management and a process to make the same. Copending U.S. Application No. 60/168844 filed on December 3, 1999, in the name of Bharat Chaudhary et al., teaches the use of flame retardants and synergists in the preparation of fabricated articles from substantially random ethylene styrene interpolymers and blends.

25 However, a significant market need still exists for a large cell, acoustically active foam with good flame retardancy. This disclosure teaches a composition and a method of preparation of such macrocellular acoustic foam having both good flame retardancy and acoustic properties, suitable for several commercial applications. The key to the invention is the selection of a low nucleating foam composition, combining it with a selected flame retardant and extruding the formulation at a specific die pressure. The formulations are based on one or more ethylene or α -olefin homopolymer resins or their blends. The

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formulation optionally includes, a second polymer component, cell-enlarging agents, and organic or inorganic flame retardant synergists.

BRIEF SUMMARY OF THE INVENTION.

One aspect of the present invention is macrocellular acoustic foam comprising:

- 5 A) one or more homopolymers of ethylene, one or more C_3 - C_{20} α -olefin polymers, or a combination thereof;
- B) one or more halogenated flame retardants;
- C) optionally, one or more polymers other than that of Component A; and
- D) optionally, one or more flame retardant synergists.

- 10 Another aspect of the present invention is a process for making macrocellular acoustic foam, such as those described below, comprising subjecting a foamable gel comprising at least one blowing agent and at least one polymeric resin composition to a die pressure greater than the prefoaming critical die pressure but less than or equal to four times that of said prefoaming critical die pressure.

- 15 Another aspect of this invention is macrocellular acoustic foams obtainable, or prepared, by the above process of this invention, particularly those comprising;

- A) one or more homopolymers of ethylene, one or more C_3 - C_{20} α -olefin polymers, or a combination thereof;
- B) one or more halogenated flame retardants;
- 20 C) optionally, one or more polymers other than that of Component A; and
- D) optionally, one or more flame retardant synergists,

as such or preferably in the form of an office partition, automotive decoupler, domestic appliance sound insulation, sound proofing panel or machine enclosure..

- 25 Another aspect of this invention is the use of the above macrocellular acoustic foam as an acoustic absorption or acoustic insulation material, particularly in environments in which fire retardancy is required.

DETAILED DESCRIPTION OF THE INVENTION.

Definitions.

5 All references herein to elements or metals belonging to a certain Group refer to the Periodic Table of the Elements published and copyrighted by CRC Press, Inc., 1989. Also any reference to the Group or Groups shall be to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups.

10 Any numerical values recited herein include all values from the lower value to the upper value in increments of one unit provided that there is a separation of at least 2 units between any lower value and any higher value. As an example, if it is stated that the amount of a component or a value of a process variable such as, for example, temperature, pressure, time and the like is, for example, from 1 to 90, preferably from 20 to 80, more preferably from 30 to 70, it is intended that values such as 15 to 85, 22 to 68, 43 to 51, 30 to 32 etc. are expressly enumerated in this specification. For values which are less than one, one unit is considered to be 0.0001, 0.001, 0.01 or 0.1 as appropriate. These are only examples of what is specifically intended and all possible combinations of numerical values between the lowest value and the highest value enumerated are to be considered to be expressly stated in this application in a similar manner.

20 The term " flame retardant " is used herein to indicate a flame retardant which can be any halogen-containing compound or mixture of compounds which imparts flame resistance to the compositions of the present invention.

The term " flame retardant synergist " is used herein to indicate inorganic or organic compounds which enhance the effectiveness of flame-retardants, especially halogenated flame retardants.

25 The term "interpolymer" is used herein to indicate a polymer wherein at least two different monomers are polymerized to make the interpolymer. This includes copolymers, terpolymers, etc.

The term "macrocellular acoustic foam" is used herein to indicate a foam having an average cell size according to ASTM D3576 of from 1.5 mm to 15 mm, with cell sizes of from 2 mm to 10 mm being preferred, from 5 mm to 10 mm being more preferred, and from

4 mm to 8 mm being particularly preferred, and which, at a thickness of 35 mm, has an average sound absorption coefficient (measured via ASTM E-1050 at 250, 500, 1000 and 2000 Hz) of greater than 0.15, preferably greater than 0.20, more preferably greater than 0.25, even more preferably greater than 0.30.

- 5 The term "prefoaming critical die pressure" is best determined empirically by observation of the foaming process, and is defined herein as the minimum die pressure at which popping is heard at the die and the resulting foam takes on a rough surface caused by premature nucleation and expansion of the foam inside the die lip.

Preparation of Foams

- 10 Excellent teachings to processes for making ethylenic polymer foam structures and processing them can be found in C. P. Park, "Polyolefin Foam", Chapter 9, Handbook of Polymer Foams and Technology, edited by D. Klempner and K. C. Frisch, Hanser Publishers, Munich, Vienna, New York, Barcelona (1991), which is incorporated here in by reference.

- 15 The present process for making the macrocellular foam involves for the most part a conventional extrusion foaming process. The foam is advantageously prepared by heating an ethylenic polymer material to form a plasticized or melt polymer material, incorporating therein a blowing agent to form a foamable gel, and extruding the gel through a die to form the foam product. Prior to mixing with the blowing agent, the polymer material is heated to a temperature at or above its glass transition temperature or melting point. The blowing agent is optionally incorporated or mixed into the melt polymer material by any means known in the art such as with an extruder, mixer, blender, or the like. The blowing agent is mixed with the melt polymer material at an elevated pressure sufficient to prevent substantial expansion of the melt polymer material and to advantageously disperse the blowing agent homogeneously therein. Optionally, a nucleator is optionally blended in the polymer melt or dry blended with the polymer material prior to plasticizing or melting. The foamable gel is typically cooled to a lower temperature to optimize physical characteristics of the foam structure. The gel is then extruded or conveyed through a die of desired shape to a zone of reduced or lower pressure to form the foam structure. The zone of lower pressure is at a pressure lower than that in which the foamable gel is maintained prior to extrusion through
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- 25

the die. The lower pressure is optionally superatmospheric or subatmospheric (vacuum), but is preferably at an atmospheric level.

However, what is critical to the process of the present invention is that the preparation of the macrocellular foam involves using a low die pressure for extrusion which is greater than the prefoaming critical die pressure but can only go as high as four times, more preferably three times, even more preferably two times the prefoaming critical die pressure.

The range of the prefoaming critical die pressure can be estimated from a calculation based on solubility data for the blowing agent in the polymer melt as a function of temperature and pressure. For interpolation or extrapolation, the Flory-Huggins equation or the Eyring and Henry equations can be used. The Flory Huggins theory provides an implicit relationship for solubility as a function of temperature and pressure and requires a trial and error solution procedure.

The Eyring equation and Henry equation provide an explicit relationship for solubility as a function of temperature and pressure that is easier to implement. The solubility of isobutane (and other blowing agents) in low density polyethylene as a function of temperature and pressure has been experimentally determined by B.I. Chaudhary & A.I. Johns and reported in Journal of Cellular Plastics, volume 34, number 4, pages 312-328 (1998). Experimental data is presented at three temperatures: 145°C, 160°C, and 200°C. Using the equations described below, the solubility curve at 108°C (foaming temperature) is predicted and the pressure corresponding to the solubility at 9% (weight), i.e. 90 mg/g polymer is read off as the prefoaming critical die pressure.

At constant pressure, the Eyring equation is given by

$$S = S_o \cdot \exp(-\Delta H/RT)$$

where S is the solubility of the gas at temperature, S_o is the solubility at the reference condition, ΔH is enthalpy and T is temperature, in K

At constant temperature, the Henry equation is given by

$$p = K \cdot S$$

where p is the partial pressure of the gas, K is a constant and S is the solubility

At a fixed pressure, the solubility of the gas in the melt at any temperature is calculated from the solubilities at the two experimental temperatures. Thus, the solubility at 108°C (foaming temperature) and say 40 bar can be calculated from the solubility's at say 145°C and
5 160°C at 40 bar, using the Eyring equation.

Knowing the solubility at 108°C and say 40 bar, the Henry equation can be used to calculate the pressure corresponding to the 9 % by weight isobutane solubility in polyethylene. This is the minimum pressure to keep the isobutane solubilized in the polymer melt and is therefore the prefoaming critical die pressure.

10 Due to scatter in the experimental data, extrapolation to 108°C resulted in varying values for the prefoaming critical die pressure, depending on the data points chosen. Thus the prefoaming critical die pressure obtained by extrapolation of the experimental data is therefore not reliable. Thus, it is recommended that the experimental procedure cited in the reference be used to generate the solubility curve at 108°C and the pressure corresponding to
15 the solubility of 9 pph isobutane be determined directly without extrapolation to obtain the prefoaming critical die pressure.

The prefoaming critical die pressure is best determined experimentally for formulations comprising not only the polymer components but also additional additives such as flame retardants, synergists and cell enlarging agents. This is typically accomplished by
20 preparing foams at several prefoaming die pressures and determining the effect of changes in the die pressure on the foam cell size and appearance. Below the prefoaming critical die pressure, the quality of the foam deteriorates sharply, rough skin is observed on the foam due to rupture of surface cells and typically a crackling noise is heard at the die due to rapid degassing of the blowing agent. At too high die pressures, the foam tends to nucleate
25 significantly causing a loss in cell size upper limit which typically corresponds to a value of up to four times, the prefoaming critical die pressure.

In another embodiment of the present invention, the resulting foam structure is optionally formed in a coalesced strand form by extrusion of the ethylenic polymer material through a multi-orifice die and wherein the die pressure for extrusion is greater than the
30 prefoaming critical die pressure but can only go as high as four times, preferably three times.

more preferably two times the prefoaming critical die pressure. The orifices are arranged so that contact between adjacent streams of the molten extrudate occurs during the foaming process and the contacting surfaces adhere to one another with sufficient adhesion to result in a unitary foam structure. The streams of molten extrudate exiting the die take the form of strands or profiles, which desirably foam, coalesce, and adhere to one another to form a unitary structure. Desirably, the coalesced individual strands or profiles should remain adhered in a unitary structure to prevent strand delamination under stresses encountered in preparing, shaping, and using the foam. Apparatuses and method for producing foam structures in coalesced strand form are seen in U.S. Pat. Nos. 3,573,152 and 4,824,720, both of which are incorporated herein by reference.

Alternatively, the resulting foam structure is conveniently formed by an accumulating extrusion process as seen in U.S. Pat. No. 4,323,528, which is incorporated by reference herein. In this process, low density foam structures having large lateral cross-sectional areas are prepared by: 1) forming under pressure a gel of the ethylenic polymer material and a blowing agent at a temperature at which the viscosity of the gel is sufficient to retain the blowing agent when the gel is allowed to expand; 2) extruding the gel into a holding zone maintained at a temperature and pressure which does not allow the gel to foam, the holding zone having an outlet die defining an orifice opening into a zone of lower pressure at which the gel foams, and an openable gate closing the die orifice; 3) periodically opening the gate; 4) substantially concurrently applying mechanical pressure by a movable ram on the gel to eject it from the holding zone through the die orifice into the zone of lower pressure, at a rate greater than that at which substantial foaming in the die orifice occurs and less than that at which substantial irregularities in cross-sectional area or shape occurs; and 5) permitting the ejected gel to expand unrestrained in at least one dimension to produce the foam structure, and 6) wherein the die pressure for extrusion is greater than the prefoaming critical die pressure where prefoaming occurs but can only go as high as four times, more preferably three times, even more preferably two times the prefoaming critical die pressure.

Blowing agents useful in making the resulting foam structure include inorganic agents, organic blowing agents and chemical blowing agents. Suitable inorganic blowing agents include carbon dioxide, nitrogen, argon, water, air, nitrogen, and helium. Organic blowing agents include aliphatic hydrocarbons having 1-6 carbon atoms, aliphatic alcohols having 1-3 carbon atoms, and fully and partially halogenated aliphatic hydrocarbons having

1-4 carbon atoms. Aliphatic hydrocarbons include methane, ethane, propane, n-butane, isobutane, n-pentane, isopentane, neopentane, and the like. Aliphatic alcohols include methanol, ethanol, n-propanol, and isopropanol. Fully and partially halogenated aliphatic hydrocarbons include fluorocarbons, chlorocarbons, and chlorofluorocarbons. Examples of fluorocarbons include methyl fluoride, perfluoromethane, ethyl fluoride, 1,1-difluoroethane (HFC-152a), 1,1,1-trifluoroethane (HFC-143a), 1,1,1,2-tetrafluoro-ethane (HFC-134a), pentafluoroethane, difluoromethane, perfluoroethane, 2,2-difluoropropane, 1,1,1-trifluoropropane, perfluoropropane, dichloropropane, difluoropropane, perfluorobutane, perfluorocyclobutane. Partially halogenated chlorocarbons and chlorofluorocarbons for use in this invention include methyl chloride, methylene chloride, ethyl chloride, 1,1,1-trichloroethane, 1,1-dichloro-1 fluoroethane (HCFC-141b), 1-chloro 1,1-difluoroethane (HCFC-142b), 1-dichloro-2,2,2-trifluoroethane (HCFC-123) and 1-chloro-1,2,2,2-tetrafluoroethane (HCFC-124). Fully halogenated chlorofluorocarbons include trichloromonofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), trichlorotrifluoroethane (CFC-113), 1,1,1-trifluoroethane, pentafluoroethane, dichlorotetrafluoroethane (CFC-114), chloroheptafluoropropane, and dichlorohexafluoropropane. Chemical blowing agents include azodicarbonamide, azodiisobutyronitrile, barium azodicarboxylate, n,n'-dimethyl-n,n'-dinitrosoterephthalamide, and benzenesulfonylhydrazide, 4,4-oxybenzene sulfonyl semicarbazide, and p-toluene sulfonyl semicarbazide trihydrazino triazine. Preferred blowing agents include propane, n-butane, isobutane, HCFC-142b, HFC-152a, carbon dioxide and mixtures of the foregoing.

The amount of blowing agent incorporated into the polymer melt material to make a foam-forming polymer gel is typically from 0.2 to 5.0, preferably from 0.5 to 3.0, and most preferably from 1.0 to 2.50 gram moles per kilogram of polymer. However, these ranges should not be taken to limit the scope of the present invention.

The foam of this invention preferably has perforation channels, more preferably a multiplicity of perforation channels extending from the at least one surface into the foam such that there is an average of at least one, preferably at least 5, more preferably at least 10, even more preferably at least 20, and even more preferably at least 30, perforation channel(s) per 10 square centimeters (cm^2) area of the at least one surface. The term "multiplicity" as

used herein means at least two. In a preferred embodiment, the foam of this invention contains at least seven perforation channels.

The perforation channels preferably have an average diameter at the at least one surface of at least 0.1 mm, more preferably at least 0.5 mm, and even more preferably at least 1 mm and preferably up to about the average cell size of the foam measured according to ASTM D 3756. One or more surfaces of the foam preferably has an average of at least four perforation channels per square centimeter extending from the at least one surface into the foam.

The polymer foam preferably has an average thickness perpendicular to the surface perforated of at least 25 mm and the polymer foam is preferably perforated to an average depth of at least 5 mm below the surface of the polymer foam.

Typically, perforation comprises puncturing the base foam with one or more pointed, sharp objects. Suitable pointed, sharp objects include needles, spikes, pins, or nails. In addition, perforation may comprise drilling, laser cutting, high pressure fluid cutting, air guns, or projectiles. A description of how to create suitable perforation channels for a different purpose, namely to accelerate release of blowing agent from the foam, is provided in U.S. Patent No. 5,585,058, which is incorporated herein by reference.

In addition, the base foam may be prepared to have elongated cells by pulling the foam during expansion. Such pulling results in elongated cells without changing or often, increasing the cell size in the horizontal direction. Thus, pulling results in an increased average cell size in the direction perpendicular to the vertical direction (EH average) and facilitates perforation.

Perforation of the base foam may be performed in any pattern, including square patterns and triangular patterns. Although the choice of a particular diameter of the sharp, pointed object with which to perforate the base foam is dependent upon many factors, including average cell size, intended spacing of perforations, pointed, sharp objects useful in the preparation of certain foams of the present invention will typically have diameters of from 1 mm to 4 mm.

Compression may be used as an additional means of opening cells. Compression may be performed by any means sufficient to exert external force to one or more surfaces of the

foam, and thus cause the cells within the foam to burst. Compression during or after perforation is especially effective in rupturing the cell walls adjacent to the channels created by perforation since a high pressure difference across the cell walls can be created. In addition, unlike needle punching, compression can result in rupturing cell walls facing in all directions, thereby creating tortuous paths desired for sound absorption.

The mechanical opening of closed-cells of the base foam lowers the airflow resistivity of the base foam by creating large-size pores in the cell walls and struts. In any event, regardless of the particular means by which it does so, such mechanical opening of closed-cells within the base thermoplastic polymer foam serves to enhance the usefulness of the foam for sound absorption and sound insulation applications.

Of course, the percentage of cells opened mechanically will depend on a number of factors, including cell size, cell shape, means for opening, and the extent of the application of the means for opening applied to the base foam.

The resulting foam structure preferably exhibits good dimensional stability. Preferred foams recover 80 or more percent of initial volume within a month with initial volume being measured within 30 seconds after foam expansion. Volume is measured by a suitable method such as cubic displacement of water.

In addition, a nucleating agent may optionally be added in order to control the size of foam cells. Preferred nucleating agents include inorganic substances such as calcium carbonate, talc, clay, titanium oxide, silica, barium sulfate, diatomaceous earth, mixtures of citric acid and sodium bicarbonate, and the like. The amount of nucleating agent employed may range from 0 to 5 parts by weight per hundred parts by weight of a polymer resin.

The resulting foam structure may be substantially noncrosslinked or uncrosslinked. The polymer material comprising the foam structure is substantially free of crosslinking.

The foam structure may also be substantially cross-linked. Cross-linking may be induced by addition of a cross-linking agent or by radiation. Induction of cross-linking and exposure to an elevated temperature to effect foaming or expansion may occur simultaneously or sequentially. If a cross-linking agent is used, it is incorporated into the polymer material in the same manner as the chemical blowing agent. Further, if a cross-linking agent is used, the foamable melt polymer material is heated or exposed to a

temperature of preferably less than 150°C to prevent decomposition of the cross-linking agent or the blowing agent and to prevent premature cross-linking. If radiation cross-linking is used, the foamable melt polymer material is heated or exposed to a temperature of preferably less than 160°C to prevent decomposition of the blowing agent. The foamable melt polymer material is extruded or conveyed through a die of desired shape to form a foamable structure. The foamable structure is then cross-linked and expanded at an elevated or high temperature (typically, 150°C-250°C) such as in an oven to form a foam structure. If radiation cross-linking is used, the foamable structure is irradiated to cross-link the polymer material, which is then expanded at the elevated temperature as described above. The present structure can advantageously be made in sheet or thin plank form according to the above process using either cross-linking agents or radiation.

The present foam structure may also be made into a continuous plank structure by an extrusion process utilizing a long-land die as described in GB 2,145,961A. In that process, the polymer, decomposable blowing agent and cross-linking agent are mixed in an extruder, heating the mixture to let the polymer cross-link and the blowing agent to decompose in a long-land die; and shaping and conducting away from the foam structure through the die with the foam structure and the die contact lubricated by a proper lubrication material

The resulting foam structure may be either closed-celled or open-celled. The open cell content will range from 0 to 100 volume % as measured according to ASTM D2856-A.

The resulting foam structure preferably has a density of less than 300, preferably less than 100, more preferably less than 60 and most preferably from 10 to 50 kilograms per cubic meter.

The macrocellular foams exhibit an average cell size of from 1.5 mm to 15 mm, with cell sizes of from 2 mm to 10 mm being preferred, from 3 mm to 10 mm being more preferred, and from 4 mm to 8 mm being particularly preferred, according to ASTM D3576. The preferred ranges of density and cell size should not be taken as limiting the scope of this invention.

The macrocellular foams made by the process of the present invention can be prepared from any combination of polymers for which the prefoaming critical die pressure can be determined. Preferably the resin to be foamed comprises an ethylene or α -olefin

homopolymer resin or a blend of one or more of said ethylene or α -olefin homopolymers.

The resin to be foamed can also comprise a blend of one or more of said ethylene or α -olefin homopolymers with a second polymer component. This second polymer component can include, but is not limited to, ethylene/ α olefin interpolymers (including polyolefin
5 elastomers, and polyolefin plastomers) or one or more substantially random interpolymers, or combinations thereof.

The α -Olefin Homopolymer

The homopolymer resins include polyethylene or C_3 - C_{20} α -olefin homopolymers or combinations thereof, preferably polyethylene or C_3 - C_{10} α -olefin homopolymers or
10 combinations thereof, most preferably interpolymers comprising polyethylene or propylene polymers, or combinations thereof. One such class of polyethylene resins is generally produced by a high pressure polymerization process using a free radical initiator resulting in the traditional long chain branched low density polyethylene (LDPE). LDPE employed in the present composition usually has a density of less than or equal to 0.935
15 g/cc (ASTM D 792) and a melt index of from 0.01 to 100, and preferably from 0.05 to 50, more preferably from 0.1 to 20 grams per 10 minutes (as determined by ASTM Test Method D 1238, Condition 190°/2.16).

The term "propylene polymer" as used herein means a polymer in which at least 50 weight percent of its monomeric units are derived directly from propylene. Suitable
20 ethylenically unsaturated monomers other than propylene that may be included in the propylene polymer, include olefins, vinylacetate, methylacrylate, ethylacrylate, methyl methacrylate, acrylic acid, itaconic acid, maleic acid, and maleic anhydride. Appropriate propylene interpolymers include random, block, and grafted copolymers or interpolymers of propylene and an olefin selected from the group consisting of ethylene, C_4 - C_{10} 1-olefins,
25 and C_4 - C_{10} dienes. Propylene interpolymers also include random terpolymers of propylene and 1-olefins selected from the group consisting of ethylene and C_4 - C_8 1-olefins. The C_4 - C_{10} 1-olefins include the linear and branched C_4 - C_{10} 1-olefins such as, for example, 1-butene, isobutylene, 1-pentene, 3-methyl-1-butene, 1-hexene, 3,4-dimethyl-1-butene, 1-heptene, 3-methyl-1-hexene, and the like. Examples of C_4 - C_{10} dienes include 1,3-
30 butadiene, 1,4-pentadiene, isoprene, 1,5-hexadiene, and 2,5-dimethyl-1,5-hexadiene. As

used herein, the term "interpolymers" means polymers derived from the reaction of two of more different monomers and includes, for example, copolymers and terpolymers.

The propylene polymer material may be comprised solely of one or more propylene homopolymers, one or more propylene copolymers, and blends of one or more of each of propylene homopolymers and copolymers. The polypropylene preferably comprises at least 70, even more preferably at least 90, and even more preferably 100, weight percent propylene monomer derived units (i.e., the propylene homopolymers are preferred).

The propylene polymer preferably has a weight average molecular weight (M_w) of at least 100,000. M_w can be measured by known procedures.

The propylene polymer also preferably has a branching index less than 1. The branching index is an approach to quantifying the degree of long chain branching selected for this particular invention. The definition of branching index and procedure for determining the same is described in column 3, line 65 to column 4, line 30, of U.S. Patent 4,916,198, which is incorporated herein by reference. The branching index is more preferably less than 0.9, and even more preferably less than 0.4.

The propylene polymer has a $\tan \delta$ value not greater than 1.5, preferably not greater than 1.2, even more preferably not greater than 1.0, and even more preferably not greater than 0.8. $\tan \delta$ may be calculated from g''/g' , where g'' is the loss modulus of the propylene polymer and g' is storage modulus of the propylene polymer melt using a 2.5 mm thick and 25 mm diameter specimen of the propylene polymer at 190 °C at a one Radian per second oscillating frequency. These parameters may be measured using a mechanical spectrometer, such as a Rheometrics Model RMS-800 available from Rheometrics, Inc., Piscataway, New Jersey, U.S.A. Further details of how to carry out this determination of the $\tan \delta$, g' and g'' values is provided in column 5, lines 59 to 64, and column 6, lines 4 to 29, of U.S. Patent 5,527,573, which is incorporated herein by reference.

In addition or in the alternative, the propylene polymer preferably has a melt tension of at least 7 centiNewtons (cN), more preferably at least 10 cN, and even more preferably at least 15 cN, and even more preferably at least 20 cN. Preferably, the propylene polymer has a melt tension not greater than 60 cN, more preferably not greater than 40 cN. The term "melt tension" as used throughout this description refers to a measurement of the

tension in cN of a strand of molten polymer material at extruded from a capillary die with an diameter of 2.1 mm and a length of 40 mm at 230°C at an extrusion speed of 20 mm/minute (min.) and a constant take-up speed of 3.14 meter/minute using an apparatus known as a Melt Tension Tester Model 2 available from Toyo Seiki Seisaku-sho, Ltd. This method for
5 determining melt tension is sometimes referred to as the "Chisso method".

In addition or in the alternative, the propylene polymer preferably has a melt strength of at least 10 centiNewtons (cN), more preferably at least 20 cN, and even more preferably at least 25 cN, and even more preferably at least 30 cN. Preferably, the propylene polymer has a melt strength not greater than 60 cN, more preferably not greater than 55 cN. The
10 term "melt strength" throughout this description refers to a measurement of the tension in cN of a strand of molten polymer material extruded from a capillary die with an diameter of 2.1 mm and a length of 41.9 mm at 190°C at a rate of 0.030 cc/sec. and stretched at a constant acceleration to determine the limiting draw force, or strength at break, using an apparatus known as a Gottfert Rheotens™ melt tension apparatus available from Gottfert, Inc.

15 The propylene polymer used in the process of the invention preferably also has a melt elongation of at least 100 percent, more preferably at least 150 percent, most preferably at least 200 percent as measured by the same Rheotens™ melt tension apparatus and general procedure described above.

The propylene polymer material preferably also has a melt flow rate of at least 0.01
20 more preferably at least 0.05, even more preferably at least 0.1 g/10 min., and even more preferably at least 0.5 g/10 min. up to 100, more preferably up to 50, even more preferably up to 20, and even more preferably up to 10, g/10 min. Throughout this description, the term "melt flow rate" refers to a measurement conducted according to American Society for Testing and Materials (ASTM) D-1238 condition 230°C/2.16 kg. (aka Condition L).

25 Preferred propylene polymers include those that are branched or lightly cross-linked. Branching (or light cross-linking) may be obtained by those methods generally known in the art, such as chemical or irradiation branching/light cross-linking. One such resin which is prepared as a branched/lightly cross-linked polypropylene resin prior to using the polypropylene resin to prepare a finished polypropylene resin product and the method of
30 preparing such a polypropylene resin is described in U.S. Patent No. 4,916,198, which is hereby incorporated by reference. Another method to prepare branched/lightly cross-linked

polypropylene resin is to introduce chemical compounds into the extruder, along with a polypropylene resin and allow the branching/lightly cross-linking reaction to take place in the extruder. This method is illustrated in U.S. Patent Nos. 3,250,731 with a polyfunctional azide, U.S. Patent 4,714,716 (and published International Application WO 99/10424) with an azidofunctional silane and EP 879,844-A1 with a peroxide in conjunction with a multi-vinyl functional monomer. The aforementioned U.S. patents are incorporated herein by reference. Irradiation techniques are illustrated by U.S. Patent Nos. 5,605,936 and 5,883,151, which are also incorporated by reference. The polymer composition used to prepare the foam preferably has a gel content of less than 10 percent, more preferably less than 5 percent, per ASTM D2765-84, Method A.

If the ethylene homopolymer is blended with the propylene polymer, the weight ratio of the propylene polymer to the ethylene homopolymer is at least 35:65.

The Second Polymer Blend Component

In addition to the olefin homopolymer component, the polymer compositions used to prepare the foams of the present invention optionally can also comprise a second polymer component, which must be foamable in its unblended state, and must also, when blended with the olefin homopolymer component, yield a macrocellular acoustic foam. The olefin homopolymer or blend component is typically the majority component of a blend with a second polymer blend component, although this depends on their relative melting points and/or Tg's. In any such blend, it is critical that the component having the highest melting point or Tg be present in an amount greater than 35 wt%, preferably greater than 40 wt %, more preferably greater than 50 wt % in the final blend

This second polymer component can comprise one or more of; heterogeneous ethylene/ α -olefin interpolymers, preferably a heterogeneous ethylene/ C_3 - C_8 α -olefin interpolymers, most preferably a heterogeneous ethylene/ octene-1 interpolymers; or homogeneous ethylene/ α -olefin interpolymers, including the substantially linear ethylene/ α -olefin interpolymers, most preferably a substantially linear ethylene/ C_3 - C_8 α -olefin interpolymers; or a substantially random interpolymers, preferably a substantially random ethylene/styrene interpolymers; or a thermoplastic olefin, preferably an ethylene/propylene rubber (EPM) or ethylene/propylene diene monomer terpolymer (EPDM); or a styrenic block copolymer, preferably styrene-butadiene (SB), styrene-isoprene (SI), styrene-

butadiene-styrene (SBS), styrene-isoprene-styrene (SIS) or styrene-ethylene-butadiene-styrene (SEBS) block copolymer, most preferably a styrene-butadiene-styrene (SBS) copolymer; or styrenic homopolymers or copolymers, preferably polystyrene, high impact polystyrene, copolymers of styrene and at least one of acrylonitrile, methacrylonitrile, maleic anhydride, or α -methyl styrene, most preferably polystyrene; or elastomers, preferably polyisoprene, polybutadiene, natural rubbers, ethylene/propylene rubbers, ethylene/propylene diene (EPDM) rubbers, styrene/butadiene rubbers, thermoplastic polyurethanes; or vinyl halide homopolymers and copolymers, preferably homopolymers or copolymers of vinyl chloride or vinylidene chloride or the chlorinated derivatives therefrom, most preferably poly (vinyl chloride) and poly (vinylidene chloride); or engineering thermoplastics, preferably poly(methylmethacrylate) (PMMA), cellulose, nylons, poly(esters), poly(acetals); poly(amides), the poly(arylate), aromatic polyesters, poly(carbonate), poly(butylene) and polybutylene and polyethylene terephthalates, most preferably poly(methylmethacrylate) (PMMA), and poly(esters); and any and all combinations thereof.

The ethylene/ α -olefin interpolymers can be further characterized by their degree of long or short chain branching and the distribution thereof. Linear olefin polymers which have an absence of long chain branching, such as the traditional linear low density polyethylene polymers (heterogeneous LLDPE) or linear high density polyethylene polymers (HDPE) made using Ziegler polymerization processes (for example, U.S. Patent No. 4,076,698 (Anderson et al.), are sometimes called heterogeneous polymers.

HDPE consists mainly of long linear polyethylene chains. The HDPE employed in the present composition usually has a density of at least 0.94 grams per cubic centimeter (g/cc) as determined by ASTM D 792, and a melt index of from 0.01 to 1000, and preferably from 0.01 to 100, more preferably from 0.05 to 50 grams per 10 minutes (as determined by ASTM Test Method D 1238, Condition 190°/2.16).

The heterogeneous LLDPE employed in the present composition generally has a density of from 0.85 to 0.94 g/cc (ASTM D 792), and melt index of from 0.01 to 1000, and preferably from 0.01 to 100, more preferably from 0.05 to 50 grams per 10 minutes (as determined by ASTM Test Method D 1238, Condition 190°/2.16). Preferably the LLDPE is an interpolymers of ethylene and one or more other α -olefins having from 3 to

18 carbon atoms, more preferably from 3-8 carbon atoms. Preferred comonomers include 1-butene, 4-methyl-1-pentene, 1-hexene, and 1-octene.

A further class is that of the uniformly branched or homogeneous polymers (e.g. homogeneous polyethylene). The homogeneous polymers contain no long chain branches and have only branches derived from the monomers (if having more than two carbon atoms). Homogeneous polymers include those made as described in U.S. Patent 3,645,992 (Elston), and those made using so-called single site catalysts in a batch reactor having relatively high olefin concentrations (as described in U.S. Patent Nos. 5,026,798 and 5,055,438 (Canich). The uniformly branched/homogeneous polymers are those polymers in which the comonomer is randomly distributed within a given interpolymer molecule and wherein the interpolymer molecules have a similar ethylene/comonomer ratio within that interpolymer.

The homogeneous LLDPE employed in the present composition generally has a density of from 0.85 to 0.94 g/cc (ASTM D 792), and a melt index of from 0.01 to 1000, and preferably from 0.01 to 100, more preferably from 0.05 to 50 grams per 10 minutes (as determined by ASTM Test Method D 1238, Condition 190°/2.16).

Preferably the LLDPE is an interpolymer of ethylene and one or more other α -olefins having from 3 to 18 carbon atoms, more preferably from 3-8 carbon atoms. Preferred comonomers include 1-butene, 4-methyl-1-pentene, 1-hexene, and 1-octene.

Further, there is the class of substantially linear olefin polymers that may advantageously be as a component (B) of the blends used to prepare the foams of the present invention. These polymers have processability similar to LDPE, but the strength and toughness of LLDPE. Substantially linear olefin polymers are disclosed in U.S. Patent Nos. 5,272,236 and 5,278,272, the entire contents of which are incorporated herein by reference.

The density of the substantially linear olefin polymers as measured in accordance with ASTM D-792 is generally from 0.85 g/cc to 0.97 g/cc, preferably from 0.85 g/cc to 0.955 g/cc, and especially from 0.85 g/cc to 0.92 g/cc and a melt index of from 0.01 to 1000, and preferably from 0.01 to 100, more preferably from 0.05 to 50 grams per 10 minutes (as determined by ASTM Test Method D 1238, Condition 190°/2.16).

Also, included are the ultra low molecular weight ethylene polymers and ethylene/ α -olefin interpolymers described in the U. S. Patent Application No. 784,683 entitled Ultra-Low Molecular Weight Polymers, filed January 22, 1997 M. J. Guest, et al., which is

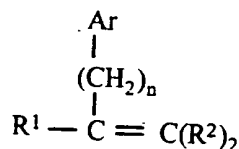
incorporated herein by reference. These ethylene/ α -olefin interpolymers have I_2 melt indices greater than 1,000, or a number average molecular weight (M_n) less than 11,000.

Especially preferred olefinic polymers comprise HDPE, heterogeneous LLDPE, homogeneous linear polyethylene, substantially linear olefin polymer, polypropylene (PP), especially isotactic polypropylene, syndiotactic polypropylene and rubber toughened polypropylenes, or ethylene-propylene interpolymers (EP), or chlorinated polyolefins (CPE), or ethylene-vinyl acetate copolymers (EVA), the polymeric ionomer compositions or ethylene-acrylic acid copolymers, or any combination thereof.

Also included in the second polymer component are the so called substantially random interpolymers which comprise polymer units derived from one or more α -olefin monomers with one or more vinyl or vinylidene aromatic monomers and/or a hindered aliphatic or cycloaliphatic vinyl or vinylidene monomers. The term substantially random as used herein means that the distribution of the monomers of said interpolymer can be described by the Bernoulli statistical model or by a first or second order Markovian statistical model, as described by J. C. Randall in POLYMER SEQUENCE DETERMINATION, Carbon-13 NMR Method, Academic Press New York, 1977, pp. 71-78. Preferably, substantially random interpolymers do not contain more than 15 percent of the total amount of vinyl or vinylidene aromatic monomer in blocks of vinyl or vinylidene aromatic monomer of more than 3 units. More preferably, the interpolymer is not characterized by a high degree of either isotacticity or syndiotacticity. This means that in the carbon-¹³ NMR spectrum of the substantially random interpolymer the peak areas corresponding to the main chain methylene and methine carbons representing either meso diad sequences or racemic diad sequences should not exceed 75 percent of the total peak area of the main chain methylene and methine carbons.

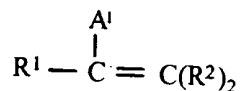
Suitable α -olefins include for example, α -olefins containing from 2 to 20, preferably from 2 to 12, more preferably from 2 to 8 carbon atoms. Particularly suitable are ethylene, propylene, butene-1, pentene-1, 4-methyl-1-pentene, hexene-1 or octene-1 or ethylene in combination with one or more of propylene, butene-1, 4-methyl-1-pentene, hexene-1 or octene-1. These α -olefins do not contain an aromatic moiety.

Suitable vinyl or vinylidene aromatic monomers which can be employed to prepare the interpolymers include, for example, those represented by the following formula:



wherein R^1 is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, preferably hydrogen or methyl; each R^2 is independently selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, preferably hydrogen or methyl; Ar is a phenyl group or a phenyl group substituted with from 1 to 5 substituents selected from the group consisting of halo, C_{1-4} -alkyl, and C_{1-4} -haloalkyl; and n has a value from zero to 4, preferably from zero to 2, most preferably zero. Exemplary vinyl or vinylidene aromatic monomers include styrene, vinyl toluene, α -methylstyrene, t-butyl styrene, chlorostyrene, including all isomers of these compounds, and the like. Particularly suitable such monomers include styrene and lower alkyl- or halogen-substituted derivatives thereof. Preferred monomers include styrene, α -methyl styrene, the lower alkyl- ($\text{C}_1 - \text{C}_4$) or phenyl-ring substituted derivatives of styrene, such as for example, ortho-, meta-, and para-methylstyrene, the ring halogenated styrenes, para-vinyl toluene or mixtures thereof, and the like. A more preferred aromatic vinyl monomer is styrene.

By the term "hindered aliphatic or cycloaliphatic vinyl or vinylidene compounds", it is meant addition polymerizable vinyl or vinylidene monomers corresponding to the formula:



wherein A^1 is a sterically bulky, aliphatic or cycloaliphatic substituent of up to 20 carbons, R^1 is selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, preferably hydrogen or methyl; each R^2 is independently selected from the group of radicals consisting of hydrogen and alkyl radicals containing from 1 to 4 carbon atoms, preferably hydrogen or methyl; or alternatively R^1 and A^1 together form a ring system. By the term "sterically bulky" is meant that the monomer bearing this substituent is normally incapable of addition polymerization by standard Ziegler-Natta polymerization catalysts at a rate comparable with ethylene polymerizations. Preferred hindered aliphatic or cycloaliphatic vinyl or vinylidene compounds are monomers in which one of the carbon atoms bearing ethylenic unsaturation is tertiary or quaternary substituted. Examples of such

substituents include cyclic aliphatic groups such as cyclohexyl, cyclohexenyl, cyclooctenyl, or ring alkyl or aryl substituted derivatives thereof, tert-butyl, norbornyl, and the like. Most preferred hindered aliphatic or cycloaliphatic vinyl or vinylidene compounds are the various isomeric vinyl- ring substituted derivatives of cyclohexene and substituted cyclohexenes, and 5-ethylidene-2-norbornene. Especially suitable are 1-, 3-, and 4-vinylcyclohexene.

Other optional polymerizable ethylenically unsaturated monomer(s) include norbornene and C₁₋₁₀ alkyl or C₆₋₁₀ aryl substituted norbornenes. Exemplary substantially random interpolymers include ethylene/styrene, ethylene/styrene/propylene, ethylene/styrene/octene, ethylene/styrene/butene, and ethylene/styrene/norbornene interpolymers.

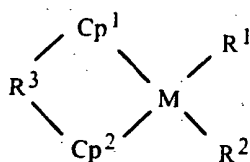
The substantially random interpolymers may be modified by typical grafting, hydrogenation, functionalizing, or other reactions well known to those skilled in the art. The polymers may be readily sulfonated or chlorinated to provide functionalized derivatives according to established techniques.

The substantially random interpolymers may also be modified by various cross-linking processes including, but not limited to peroxide-, silane-, sulfur-, radiation-, or azide-based cure systems. A full description of the various cross-linking technologies is described in copending U.S. Patent Application Nos. 08/921,641, now issued as US-A-5,869,591, and 08/921,642, now issued as US-A-5,977,271, both filed on August 27, 1997, the entire contents of both of which are herein incorporated by reference. Dual cure systems, which use a combination of heat, moisture cure, and radiation steps, may be effectively employed. Such dual cure systems are disclosed and claimed in U. S. Patent Application Serial No. 536,022, filed on September 29, 1995, in the names of K. L. Walton and S. V. Karande, now issued as US-A-5,911,940, which is incorporated herein by reference. For instance, it may be desirable to employ peroxide crosslinking agents in conjunction with silane crosslinking agents, peroxide crosslinking agents in conjunction with radiation, sulfur-containing crosslinking agents in conjunction with silane crosslinking agents, etc. The substantially random interpolymers may also be modified by various cross-linking processes including, but not limited to the incorporation of a diene component as a termonomer in its preparation and subsequent cross linking by the aforementioned methods and further methods including vulcanization via the vinyl group using sulfur for example as the cross linking agent.

The substantially random interpolymers include the pseudo-random interpolymers as described in EP-A-0,416,815 by James C. Stevens et al. and US Patent No. 5,703,187 by Francis J. Timmers, both of which are incorporated herein by reference in their entirety. The substantially random interpolymers also include the substantially random terpolymers as described in US Patent No. 5,872,201 which is incorporated herein by reference in their entirety. The substantially random interpolymers are best prepared by polymerizing a mixture of polymerizable monomers in the presence of one or more metallocene or constrained geometry catalysts in combination with various cocatalysts. Preferred operating conditions for the polymerization reactions are pressures from atmospheric up to 3000 atmospheres and temperatures from -30°C to 200°C. Polymerizations and unreacted monomer removal at temperatures above the autopolymerization temperature of the respective monomers may result in formation of some amounts of homopolymer polymerization products resulting from free radical polymerization.

Examples of suitable catalysts and methods for preparing the substantially random interpolymers are disclosed in EP-A-416,815; EP-A-514,828; EP-A-520,732; and EP-B-705,269; as well as U.S. Patents: 5,055,438; 5,057,475; 5,096,867; 5,064,802; 5,132,380; 5,189,192; 5,321,106; 5,347,024; 5,350,723; 5,374,696; 5,399,635; and 5,470,993, all of which patents and applications are incorporated herein by reference.

The substantially random α -olefin/ vinyl or vinylidene aromatic interpolymers can also be prepared by the methods described in JP 07/278230 employing compounds shown by the general formula



where Cp^1 and Cp^2 are cyclopentadienyl groups, indenyl groups, fluorenyl groups, or substituents of these, independently of each other; R^1 and R^2 are hydrogen atoms, halogen atoms, hydrocarbon groups with carbon numbers of 1-12, alkoxyl groups, or aryloxy groups, independently of each other; M is a group IV metal, preferably Zr or Hf, most preferably Zr; and R^3 is an alkylene group or silanediyl group used to cross-link Cp^1 and Cp^2

The substantially random α -olefin/ vinyl or vinylidene aromatic interpolymers can also be prepared by the methods described by John G. Bradfute et al. (W. R. Grace & Co.) in WO 95/32095; by R. B. Pannell (Exxon Chemical Patents, Inc.) in WO 94/00500; and in Plastics Technology, p. 25 (September 1992), all of which are incorporated herein by reference in their entirety.

Also suitable are the substantially random interpolymers which comprise at least one α -olefin/vinyl aromatic/vinyl aromatic/ α -olefin tetrad disclosed in WO 98/0999. These interpolymers contain additional signals with intensities greater than three times the peak to peak noise. These signals appear in the chemical shift range 43.70-44.25 ppm and 38.0-38.5 ppm. Specifically, major peaks are observed at 44.1, 43.9 and 38.2 ppm. A proton test NMR experiment indicates that the signals in the chemical shift region 43.70-44.25 ppm are methine carbons and the signals in the region 38.0-38.5 ppm are methylene carbons.

Further preparative methods for the interpolymers used in the present invention have been described in the literature. Longo and Grassi (Makromol. Chem., Volume 191, pages 2387 to 2396 [1990]) and D'Anniello et al. (Journal of Applied Polymer Science, Volume 58, pages 1701-1706 [1995]) reported the use of a catalytic system based on methylalumoxane (MAO) and cyclopentadienyltitanium trichloride (CpTiCl_3) to prepare an ethylene-styrene copolymer. Xu and Lin (Polymer Preprints, Am. Chem. Soc., Div. Polym. Chem.) Volume 35, pages 686,687 [1994]) have reported copolymerization using a $\text{MgCl}_2/\text{TiCl}_4/\text{NdCl}_3/\text{Al}(\text{iBu})_3$ catalyst to give random copolymers of styrene and propylene. Lu et al (Journal of Applied Polymer Science, Volume 53, pages 1453 to 1460 [1994]) have described the copolymerization of ethylene and styrene using a $\text{TiCl}_4/\text{NdCl}_3/\text{MgCl}_2/\text{Al}(\text{Et})_3$ catalyst. Sernetz and Mulhaupt, (Macromol. Chem. Phys., v. 197, pp. 1071-1083, 1997) have described the influence of polymerization conditions on the copolymerization of styrene with ethylene using $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(\text{N-tert-butyl})\text{TiCl}_2/\text{methylaluminoxane}$ Ziegler-Natta catalysts. Copolymers of ethylene and styrene produced by bridged metallocene catalysts have been described by Arai, Toshiaki and Suzuki (Polymer Preprints, Am. Chem. Soc., Div. Polym. Chem.) Volume 38, pages 349, 350 [1997]) and in United States patent number 5,652,315, issued to Mitsui Toatsu Chemicals, Inc. The manufacture of α -olefin/vinyl aromatic monomer interpolymers such as propylene/styrene and butene/styrene are described in United States patent number 5,244,996, issued to Mitsui Petrochemical Industries Ltd or United States patent number 5,652,315 also issued to Mitsui Petrochemical Industries Ltd or

as disclosed in DE 197 11 339 A1 and U.S. patent No. 5,883,213 to Denki Kagaku Kogyo KK. All the above methods disclosed for preparing the interpolmer component are incorporated herein by reference. Also, the random copolymers of ethylene and styrene as disclosed in Polymer Preprints Vol 39, No. 1, March 1998 by Toru Aria et al. can also be employed as blend components for the foams of the present invention.

The substantially random interpolymers usually contain from 0.5 to 65, preferably from 1 to 55, more preferably from 1 to 50 mole percent of at least one vinyl or vinylidene aromatic monomer and/or hindered aliphatic or cycloaliphatic vinyl or vinylidene monomer and from 35 to 99.5, preferably from 45 to 99, more preferably from 50 to 99 mole percent of ethylene and/or at least one aliphatic α -olefin having from 3 to 20 carbon atoms.

The substantially random interpolmer(s) applicable to the present invention can have a melt index of from 0.01 to 1000, and preferably from 0.01 to 100, more preferably from 0.05 to 50 grams per 10 minutes (as determined by ASTM Test Method D 1238, Condition 190°/2.16).

While preparing the substantially random interpolmer, an amount of atactic vinyl or vinylidene aromatic homopolymer may be formed due to homopolymerization of the vinyl or vinylidene aromatic monomer at elevated temperatures. The presence of vinyl or vinylidene aromatic homopolymer is in general not detrimental for the purposes of the present invention and can be tolerated. The vinyl or vinylidene aromatic homopolymer may be separated from the interpolmer, if desired, by extraction techniques such as selective precipitation from solution with a non solvent for either the interpolmer or the vinyl or vinylidene aromatic homopolymer. For the purpose of the present invention it is preferred that no more than 20 weight percent, preferably less than 15 weight percent, most preferably less than 10 weight percent based on the total weight of the interpolymers of atactic vinyl or vinylidene aromatic homopolymer is present.

Most preferred as the second polymer component are the substantially random interpolymers such as those marketed by The Dow Chemical Company under the INDEX™ tradename, the polyolefin plastomers, such as those marketed by The Dow Chemical Company under the AFFINITY™ tradename and polyethylene elastomers, such as those marketed by Du Pont Dow Elastomers LLC under the ENGAGE™ tradename.

Flame Retardant

As the foam will be used as acoustical insulation in buildings, it will also contain a flame retardant which functions to extinguish flames or at least slow the spread of fire in the foam. Suitable flame retardants are well-known in the art and include but are not limited to

5 hexahalodiphenyl ethers, tetrabromobisphenol A bis (2,3-dibromopropyl ether)

octahalodiphenyl ethers, decahalodiphenyl ethers, decahalobiphenyl ethanes, 1,2-bis(trihalophenoxy)ethanes, 1,2-bis(pentahalophenoxy)ethanes, hexahalocyclododecane, a tetrahalobisphenol-A, ethylene(N, N')-bis-tetrahalophthalimides, tetrahalophthalic anhydrides, hexahalobenzenes, halogenated indanes, halogenated phosphate esters,

10 halogenated paraffins, halogenated polystyrenes, and polymers of halogenated bisphenol-A and epichlorohydrin, or mixtures thereof. Preferably, the flame retardant is a bromine or chlorine containing compound. The halogenated flame-retardants may include one or more of hexabromocyclododecane (HBCD), tetrabromobisphenol-A- (TBBA), chlorowax and may

15 be used with or without flame retardant synergists. Commercially available products suitable for use as flame retardants in the present invention include PE-68™ (a trademark and product of the Great Lakes Chemical Corporation). Suitable flame retardants are well known, and include brominated organic compounds such as are described in US-A- 4,446,254 and US-A- 5,171,757, the entire contents of which are herein incorporated by reference. For foams, the halogen content in the final foams should be 0.05-20 wt%,

20 preferably 0.1-15 wt% and most preferably 0.2-10 wt%.

In a preferred embodiment, the flame retardant is a hexahalocyclododecane, preferably hexabromocyclododecane (HBCD), or tetrabromobisphenol A bis (2,3-dibromopropyl ether), PE™-68, or a combination with any other halogenated or non-halogenated flame-retardants, which can include, but are not limited to phosphorous based

25 flame retardants such as triphenyl phosphate and encapsulated red phosphorous.

In the case of halogenated flame retardants, preferred loadings or amounts depend on the application and the desired level of flame retardants but are those which typically yield halogen contents of 0.05 to 20 phr in foamed structures

Flame Retardant Synergist

Optionally a flame retardant synergist may be added along with the flame retardant. Examples of inorganic flame retardant synergists include, but are not limited to, metal oxides, e.g. iron oxide, tin oxide, zinc oxide, aluminum trioxide, alumina, antimony trioxide and antimony pentoxide, bismuth oxide, molybdenum trioxide, and tungsten trioxide, boron compounds such as zinc borate, antimony silicates, zinc stannate, zinc hydroxystannate, ferrocene and mixtures thereof. Examples of organic flame retardant synergists include, but are not limited to organic peroxides, such as dicumyl peroxide and polycumyl peroxide. Synergistic combinations, such as mixtures of one or more halogenated compounds and one or more flame retardant synergists, typically are used preferably at a ratio of 0.25 to 25, preferably 0.5 to 15, more preferably from 0.5 to 10 parts by weight flame retardant halogen to 1 part by weight of flame retardant synergist.

Stability Control Agent or Cell Size Enlarging Agent

A stability control agent or cell size enlarging agent is optionally added to the present foam to enhance dimensional stability. Preferred agents include amides and esters of C10-24 fatty acids. Such agents are seen in U.S. Pat. Nos. 3,644,230 and 4,214,054, which are incorporated herein by reference. Most preferred agents include stearyl stearamide, glycerol monostearate (available from ICI Americas Inc., under the trademark Atmer™ 129), glycerol monobehenate, and sorbitol monostearate. Typically, such stability control agents are employed in an amount ranging from 0.1 to 10 parts per hundred parts of the polymer.

Other Additives.

Additives such as antioxidants such as hindered phenols (e.g., Irganox™ 1010), and phosphites (e.g., Irgafos™ 168) both of which are trademarks of and available from the Ciba Geigy corporation), U.V. Stabilizers, cling additives (e.g., polyisobutylene), antiblock additives, colorants, pigments, fillers, acid scavengers (including, but not limited to, zeolite, organic carboxylates and hydrotalcite) and the like can optionally also be included in the compositions and fabricated articles of the present invention, to the extent that they do not interfere with their enhanced properties.

The additives are advantageously employed in functionally equivalent amounts known to those skilled in the art. For example, the amount of antioxidant employed is that amount which prevents the polymer or polymer blend from undergoing oxidation at the temperatures and environment employed during storage and ultimate use of the polymers.

- 5 Such amount of antioxidants is usually in the range of from 0.01 to 10, preferably from 0.05 to 5, more preferably from 0.1 to 2 percent by weight based upon the weight of the polymer or polymer blend.

- 10 Similarly, the amounts of any of the other enumerated additives are the functionally equivalent amounts such as the amount to render the polymer or polymer blend antiblocking, to produce the desired amount of filler loading to produce the desired result, to provide the desired color from the colorant or pigment. Such additives are advantageously employed in the range of from 0 to 50, preferably from 0 to 35, more preferably from 0 to 20 percent by weight based upon the weight of the polymer or polymer blend.

- 15 Preferred examples of fillers are talc, carbon black, carbon fibers, calcium carbonate, alumina trihydrate, glass fibers, marble dust, cement dust, clay, feldspar, silica or glass, fumed silica, alumina, magnesium oxide, magnesium hydroxide, antimony oxide, zinc oxide, barium sulfate, aluminum silicate, calcium silicate, titanium dioxide, titanates, glass microspheres or chalk. Of these fillers, barium sulfate, talc, calcium carbonate, silica/glass, glass fibers, alumina and titanium dioxide, and mixtures thereof are preferred. The most
20 preferred inorganic fillers are talc, calcium carbonate, barium sulfate, glass fibers or mixtures thereof. These fillers could be employed in amounts from 0 to 90, preferably from 0 to 80, more preferably from 0 to 70 % by weight based on the weight of the polymer or polymer blend.

- 25 One type of additive found useful in the polymer compositions used to prepare the foams of the present invention are lubricating agents. Such additives are better known by a variety of more common names such as slip agent or release agent which seem to depend upon the particular property modification contemplated for the additive. Illustrative lubricating agents, preferably solid lubricating agents, include organic materials such as silicones, particularly dimethylsiloxane polymers, fatty acid amides such as ethylene bis
30 (stearamides), oleamides and erucamide; and metal salts of fatty acids such as zinc, calcium, or lead stearates. Also suitable are inorganic materials such as talc, mica, fumed silica and

calcium silicate. Particularly preferred are the fatty acid amides, oleamides, and erucamide. Quantities of lubricating agent of from 0 to 5 % by weight based on the total weight of the mixture are satisfactory, more preferred are quantities of from 0 to 4 % by weight.

Applications for the macrocellular flame resistant acoustic compositions of the present invention include articles made by all the various extrusion processes. Such articles may be used in automotive and other transportation devices, building and construction, household and garden appliances, power tool and appliance and electrical supply housing, connectors, and aircraft as acoustic systems for sound absorption and insulation. The materials are especially suited to applications where, in addition to meeting the relevant acoustic performance standards, they must also meet any applicable fire test codes, for example office partitions, automotive decouplers, domestic appliance sound insulation, and sound proofing panels and machine enclosures.

The foams of the present invention have excellent acoustic absorption capabilities. One way to measure the ability to absorb sound is to measure the acoustic absorption coefficient of the foam according to ASTM E-1050 at 25, 500, 1000 and 2000 Hz and then calculate the arithmetic average of those sound absorption coefficients. When that determination is made with the foams of the present invention, the average sound absorption coefficient is greater than 0.15, preferably greater than 0.20, more preferably greater than 0.25, even more preferably greater than 0.30. Thus the foams of this invention are useful for absorbing sound in the range from 250 to 2000 Hz such that the sound absorption capability is equivalent to the foregoing preferred average sound absorption coefficients. For example, the foam may be located in the presence of a sound intensity of at least 50 decibels, such as on a vehicle equipped with a combustion engine.

The foregoing list merely illustrates a number of suitable applications. Skilled artisans can readily envision additional applications without departing from the scope or spirit of the present invention.

The following examples illustrate, but do not in any way limit the scope of the present invention.

EXAMPLES.

Test Methods.a) Melt Flow Measurements.

The molecular weight of the polymer compositions for use in the present invention is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190°C/2.16 kg (formally known as "Condition (E)" and also known as I₂) was determined. Melt index is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear.

10 b) Styrene Analyses

Interpolymer styrene content and the concentration of atactic polystyrene homopolymer impurity in the ESI interpolymers was determined using proton nuclear magnetic resonance (¹H NMR). All proton NMR samples were prepared in 1, 1, 2, 2-tetrachloroethane-d₂ (tce-d₂). The resulting solutions contained approximately 1 - 3 weight percent polymer. The interpolymers were weighed directly into 5-mm sample tubes. A 0.75-ml aliquot of tce-d₂ was added by syringe and the tube sealed with a tight-fitting cap. The samples were heated at 85°C to soften the interpolymer. To provide mixing, the capped samples were occasionally brought to reflux using a heat gun.

Proton NMR spectra were accumulated with the sample probe at 80°C, and referenced to the residual protons of tce-d₂ at 5.99 ppm. Data was collected in triplicate on each sample using the following instrumental conditions:

Sweep width, 5000 hz

Acquisition time, 3.002 sec

Pulse width, 8 μsec

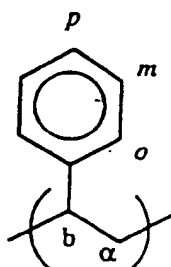
Frequency, 300 mhz

Delay, 1 sec

Transients, 16

The total analysis time per sample was 10 minutes.

Initially, a spectrum for a sample of polystyrene (192,000 M_w) was acquired. Polystyrene has five different types of protons that are distinguishable by proton NMR. In Figure 1, these protons are labeled b, branch; α, alpha; o, ortho; m, meta; p, para, as shown in figure 1. For each repeating unit in the polymer, there are one branch proton, two-alpha protons, two ortho protons, two meta protons and one para proton.



The NMR spectrum for polystyrene homopolymer includes a resonance centered around a chemical shift of 7.1 ppm, which is believed to correspond to the three ortho and para protons. The spectrum also includes another peak centered around a chemical shift of 6.6 ppm. That peak corresponds to the two meta protons. Other peaks at about 1.5 and 1.9 ppm correspond to the three aliphatic protons (alpha and branch).

The relative intensities of the resonances for each of these protons were determined by integration. The integral corresponding to the resonance at 7.1 ppm was designated PS_{7.1} below. That corresponding to the resonance at 6.6 ppm was designated PS_{6.6}, and that corresponding to the aliphatic protons (integrated from 0.8-2.5 ppm) was designated PS_{al}. The theoretical ratio for PS_{7.1}: PS_{6.6}: PS_{al} is 3:2:3, or 1.5:1:1.5. For atactic polystyrene homopolymer, all spectra collected had the expected 1.5: 1: 1.5 integration ratio. An aliphatic ratio of 2 to 1 is predicted based on the protons labeled α and b respectively in figure 1. This ratio was also observed when the two aliphatic peaks were integrated separately. Further, the ratio of aromatic to aliphatic protons was measured to be 5 to 3, as predicted from theoretical considerations.

The ¹H NMR spectrum for the ESI interpolymers was then acquired. This spectrum showed resonances centered at about 7.1 ppm, 6.6 ppm and in the aliphatic region.

However, the 6.6 ppm peak was relatively much weaker for the ESI interpolymer than for the polystyrene homopolymer. The relative weakness of this peak is believed to occur because the meta protons in the ESI copolymer resonate in the 7.1 ppm region. Thus, the only protons that produce the 6.6 ppm peak are meta protons associated with atactic polystyrene homopolymer that is an impurity in the ESI. The peak centered at about 7.1 ppm thus includes ortho, meta and para protons from the aromatic rings in the ESI interpolymer, as well as the ortho and para protons from the aromatic rings in the polystyrene homopolymer impurity. The peaks in the aliphatic region include resonances of aliphatic protons from both the ESI interpolymer and the polystyrene homopolymer impurity.

Again, the relative intensities of the peaks were determined by integration. The peak centered around 7.1 ppm is referred to below as $I_{7.1}$, that centered around 6.6 ppm is $I_{6.6}$ and that in the aliphatic regions is I_{al} .

$I_{7.1}$ includes a component attributable to the aromatic protons of the ESI interpolymer and a component attributable to the ortho and para protons of the aromatic rings of the polystyrene homopolymer impurity. Thus,

$$I_{7.1} = I_{c7.1} + I_{ps7.1}$$

where $I_{c7.1}$ is the intensity of the 7.1 ppm resonance attributable to the aromatic protons in the interpolymer and $I_{ps7.1}$ is the intensity of the 7.1 ppm resonance attributable to the ortho and meta protons of the polystyrene homopolymer.

From theoretical considerations, as confirmed by the ^1H NMR spectrum of the polystyrene homopolymer, the intensity of the 7.1 ppm resonance attributable to the polystyrene homopolymer impurity ($I_{ps7.1}$), equals 1.5 times the intensity of the 6.6 ppm resonance. This provides a basis for determining $I_{c7.1}$ from measured values, as follows:

$$I_{c7.1} = I_{7.1} - 1.5(I_{6.6}).$$

Similarly, I_{al} can be resolved into resonances attributable to the ESI and the polystyrene homopolymer impurity using the relationship

$$I_{al} = I_{cal} + I_{psal}$$

wherein I_{cal} is the intensity attributable to the aliphatic protons on the interpolmer and I_{psal} is the intensity attributable to the aliphatic protons of the polystyrene homopolymer impurity. Again, it is known from theoretical considerations and the spectrum from the atactic polystyrene homopolymer that I_{psal} will equal 1.5 times $I_{6.6}$. Thus the following relationship provides a basis for determining I_{cal} from measured values:

$$I_{cal} = I_{al} - 1.5(I_{6.6}).$$

The mole percent ethylene and styrene in the interpolmer are then calculated as follows:

$$s_c = I_{c7.1}/5$$

$$e_c = (I_{cal} - (3 \times s_c))/4$$

$$E = e_c/(s_c + e_c), \text{ and}$$

$$S = s_c/(s_c + e_c),$$

wherein E and S are the mole fractions of copolymerized ethylene and styrene, respectively, contained in the interpolmer.

Weight percent ethylene and styrene were calculated using the equations

$$\text{Wt \% E} = \frac{100 \% \times 28 E}{(28 E + 104 S)} \quad \text{and}$$

$$\text{Wt\% S} = \frac{100 \% \times 104 S}{(28 E + 104 S)}$$

The weight percent of polystyrene homopolymer impurity in the ESI sample was then determined by the following equation:

$$\text{Wt\% PS} = \frac{100\% \times \text{Wt\% S} \times (I_{6.6}/2S)}{100 - [\text{Wt\% S} \times (I_{6.6}/2S)]}$$

The total styrene content was also determined by quantitative Fourier transform infrared spectroscopy (FTIR).

Materials Used to Prepare the Foams of the Present Invention.

- 5 1. LDPE 1 is commercially available as LDPE 400R which is a low density polyethylene (LDPE) with a density of 0.925 g/cm³ and melt index of 1.0 dg/min and available from The Dow Chemical Company.
2. LDPE 2 is commercially available as LDPE 620i which is a low density polyethylene (LDPE) with a density of 0.924 g/cc and melt index of 1.8 dg/min (according to ASTM
10 D1238, 190°C/2.16 kg) and available from The Dow Chemical Company.
3. ESI 1 is commercially available as DS201 which is a substantially random ethylene styrene interpolymers (ESI) with a nominal styrene content of 37.5 mol % (69 wt %) and melt index of 1 dg/min (according to ASTM D1238, 190°C/2.16 kg) and available from The Dow Chemical Company.
- 15 4. HMS PP 1 is commercially available as Profax PF814 which is a high melt strength polypropylene with a melt index of 3 dg/min (according to ASTM D1238, 230°C/2.16 kg) and available from Montell.
5. PE-68TM is a brominated fire retardant having 68 wt % bromine content (tetrabromobisphenol A bis (2,3-dibromopropyl ether) 30% concentrate in LDPE) and is
20 a trademark of and available from The Great Lakes Chemical Corporation.
6. TRUTINTTM 50 is antimony trioxide, SbO₃ of average particle size of 3 microns (used as an 80% concentrate in LDPE) and is a trademark of and available from The Great Lakes Chemical Corporation.
7. TMSTM is antimony trioxide, SbO₃ of average particle size of 1.5 microns (used as an
25 80% concentrate in LDPE) and is a trademark of and available from The Great Lakes Chemical Corporation.
8. CHLOREZTM 700 is chlorinated paraffin containing 70 wt % chlorine and is a trademark of and available from the Dover Chemical Corporation.

9. CHLOREZ™ 760 is chlorinated paraffin containing 74 wt % chlorine and is a trademark of and available from the Dover Chemical Corporation.
10. SAYTEX™ HP-900 is hexabromocyclododecane containing about 75 wt % bromine and is a trademark of and available from the Albemarle Corporation.

5

Example 1

This example illustrates the experimental method for determining the critical prefoaming die pressure a flame retardant polyethylene formulation. The foams listed in Table 1 were prepared in commercial extrusion equipment. The laboratory scale single screw extruder consisted of a feeding zone for solid additives and resins, a melting zone and a metering zone. In addition, there was a mixing zone with a port to inject the blowing agent and liquid additives, a cooling zone to uniformly cool the melt to the foaming temperature and a die body. The foaming temperature is the optimal gel temperature for foaming when the melt strength is high enough to stabilize the foam and prevent cell collapse. The melt is extruded through a die to room temperature and pressure to expand the gel and stabilize the resulting foam.

Low density polyethylene (LDPE 1) with a density of 0.925 g/cm³ and melt index of 1.0 dg/min (according to ASTM D1238, 190°C/2.16 kg) was fed from a feed hopper to the extruder. The levels of additives used in the formulation are reported in parts by weight per hundred parts by weight of the polymer resin blend (pph). The following additives were added : 0.3 pph glycerol monostearate, 4 pph of the brominated flame retardant (PE-68, tetrabromobisphenol A bis (2,3-dibromopropyl ether) 30% concentrate in LDPE) and 2 pph of the synergist (Trutint™ 50, antimony trioxide 80% concentrate in LDPE). Isobutane at 9 pph was injected into the mixing zone. The temperature of the cooling zone and die block was gradually reduced to the foaming temperature range to produce stable foam. At a die temperature of 108°C, the die opening was changed to vary the pressure at the die. The results of the change in die pressure on cell size and foam appearance are shown in Table 1. At high die pressure (>3000 kPa), the foam nucleated significantly and cell size was small. As the die pressure was reduced, the foam quality improved and the cell size became larger. Finally, at the prefoaming pressure, the quality of the foam deteriorated sharply (very rough skin due to rupture of surface cells) and a crackling noise was heard at the die due to rapid

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degassing of the blowing agent. The prefoaming critical die pressure this formulation is 650 kPa.

Table 1

Example #	Die pressure, kPa	Die opening ¹ , mm	Average cell size ² , mm	Comments
Ex 1	3530	0.82	4.37	Collapsed foam
Ex 1	3060	0.88	4.01	Slight collapsed foam
Ex 1	2590	1.00	4.85	Slight collapsed foam
Ex 1	2420	1.10	5.58	Slight collapsed foam
Ex 1	2030	1.28	5.02	Slight collapsed foam
Ex 1	1850	1.32	5.74	Slight collapsed foam
Ex 1	1680	1.52	6.13	Moderate quality foam
Ex 1	1390	1.64	6.46	Good quality foam
Ex 1	1250	1.76	6.97	Good quality foam
Ex 1	1180	2.00	8.52	Good quality foam, big cells
Ex 1	980	2.20	7.87	Good quality foam, big cells
Ex 1	920	2.20	8.23	Good quality foam, big cells
Ex 1	830	2.36	11.59	Good quality foam, big cells
Ex 1	760	2.50	11.95	Good quality foam, big cells
Ex 1	650	2.64	10.13	Start of prefoaming, rough skin
Ex 1	490	2.90	10.08	Significant prefoaming, very rough skin

¹ die width: 6 mm

² 3-d average cell size measured by ASTM D3576

Example 2

This example also illustrates the experimental method for determining the prefoaming critical die pressure for a flame retardant polyethylene formulation.

A formulation similar to that used in Example 1 was foamed using a higher level of glycerol mono stearate (GMS). The levels of additives used in the formulation are reported in parts by weight per hundred parts by weight of the polymer resin blend (pph). The level of GMS used was 1.3 pph. All other process conditions were the same as Example 1. The

foaming temperature was 108°C. The prepared foams are listed in Table 2. In this case, the prefoaming critical die pressure for this formulation is between 350 kPa and 720 kPa.

Table 2

Example #	Die pressure, kPa	Die opening ¹ , mm	Average cell size ² , mm	Comments
Ex 2	1220	1.54	5.76	Slightly collapsed foam
Ex 2	940	1.80	6.77	Moderate quality foam
Ex 2	820	1.94	7.17	Good quality foam, big cells
Ex 2	720	2.16	8.89	Good quality foam, big cells
Ex 2	350	3.00	n.d. ³	Prefoaming, rough skin surface

¹ die width: 6 mm

5 ² 3-d average cell size measured by ASTM D3576

³ cell size not measured due to very poor quality foam

Example Three

10 The following example also illustrates the experimental method for determining the prefoaming critical die pressure for a non flame retardant polyethylene formulation. A formulation similar to that used in Example 2 without the brominated flame retardant and the synergist. The foaming temperature was 108°C, all other process conditions were the same as before. The prepared foams are listed in Table 3. In this case, the prefoaming critical die pressure for this formulation is 760 kPa.

Table 3

Example #	Die pressure, kPa	Die opening ¹ , mm	Average cell size ² , mm	Comments
Ex 3	3530	0.78	7.02	Slightly collapsed foam
Ex 3	3260	0.82	6.75	Slightly collapsed foam
Ex 3	2830	0.93	7.22	Slightly collapsed foam
Ex 3	2460	1	8.58	Moderate quality foam
Ex 3	2210	1.08	8.58	Moderate quality foam
Ex 3	1900	1.25	8.52	Moderate quality foam
Ex 3	1620	1.4	8.59	Good quality foam
Ex 3	1480	1.47	9.99	Good quality foam
Ex 3	1390	1.62	9.78	Good quality foam
Ex 3	1200	1.72	9.69	Good quality foam
Ex 3	940	1.9	11.05	Good quality foam, big cells
Ex 3	920	2	9.49	Good quality foam, big cells
Ex 3	760	2.2	10.6	Start of prefoaming, popping sound at die
Ex 3	630	2.5	10.89	Rough skin on the edges
Ex 3	590	2.7	11.25	Rough skin on the edges
Ex 3	530	3	10.8	Significant prefoaming, very rough skin

¹ die width: 6 mm² 3-d average cell size measured by ASTM D3576

Example 4

This example describes the formulation and the process conditions to make large cell acoustic foam with flame retardants and synergists.

5 The foams were prepared in commercial extrusion equipment. The pilot scale single screw extruder consisted of a feeding zone for solid additives and resins, a melting zone and a metering zone. In addition, there was a mixing zone with a port to inject the blowing agent and liquid additives, a cooling zone to uniformly cool the melt to the foaming temperature and a die body. A gear pump between the metering and mixing zones stabilized the melt flow rate. The foaming temperature is the optimal gel temperature for foaming when the
10 melt strength is high enough to stabilize the foam and prevent cell collapse. The melt is extruded through a die to room temperature and pressure to expand the gel and stabilize the resulting foam.

For this Example 4, low density polyethylene with a density of 0.925 g/cm³ and melt index of 1.0 dg/min (according to ASTM D1238, 190°C/2.16 kg) was fed to the extruder.
15 The levels of additives used in the formulation are reported in parts by weight per hundred parts by weight of the polymer resin blend (pph). For the comparative foam (Comp Ex 1) the following additive was used: 0.1 pph Irganox 1010 antioxidant (Tetrakis [methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)] methane. Isobutane at 8.5 pph was injected into the mixing zone and glycerol monostearate at 1.5 pph was melt injected. For the flame retardant
20 foam of Example 4, the following ingredients were added to the formulation : 5 pph of the brominated flame retardant (PE-68, tetrabromobisphenol A bis (2,3-dibromopropyl ether) 30% concentrate in LDPE) and 1.4 pph of the synergist (TMSTM antimony trioxide 1.5 micron average particle size 80% concentrate in LDPE).

The gel residence time in the extrusion line was 45 min. The gel temperature was the
25 highest in the mixing zone (200°C) and the gel pressure was highest at the gear pump outlet (18540 kPa). The hot gel was cooled to the foaming temperature (104°C). The gel temperature of the adjustable die (50 mm wide x 3.3 mm high) was maintained at 104°C and the gel pressure at the die was kept at 1300 kPa. Note the die pressure is approximately 2X the prefoaming critical die pressure. Macrocellular foam of excellent quality was obtained.

For the comparative foam (Comp Ex 1) made with no flame retardant package, the average cell size was 11.7 mm and the fresh density was 47.8 kg/m³.

For the foam of Example 4 made with the flame retardant package, the average cell size was 10.4 mm and the fresh density was 33.5 kg/m³.

- 5 The comparative foam (Comp Ex 1) failed the DIN-4102 B2 flame test and the UL-94 flame test. The flame retardant (Example 4) foam passed the DIN-4102 test with B2 rating (with paper burning) and passed the UL-94 test with 94 HF-2 rating (with burning droplets).

- The comparative (Comp Ex 1) and the flame retardant foam (Example 4) both with skin, no perforations and 25 mm thickness were tested for acoustic performance using ASTM E-
10 1050 (Impedance Tube Method). The acoustic results, tabulated below, show that the comparative (Comp Ex 1) and the flame retardant foam (Example 4) are very comparable.

Table 4

Sample	Sound absorption coefficients (SAC)					Max SAC (0-4000 Hz)		Average
	250 Hz	500 Hz	1000 Hz	2000 Hz	4000 Hz	SAC max	Frequency ¹	
Comp Ex 1	0.075	0.45	0.7	0.35	0.55	0.825	800	0.39
Example 4	0.075	0.35	0.75	0.425	0.4	0.825	800	0.40

¹ Frequency corresponding to the maximum sound absorption

- ² Average SAC is the mean SAC of the following frequencies: 250 Hz, 500
15 Hz, 1000 Hz, and 2000 Hz

Example 5

This example details the effect of nucleators that are used in the formulation on foam cell size and hence acoustic properties.

- The formulation was made in the same commercial extrusion equipment as described
20 in Example 4. For this example, a 85/15 wt% blend of low density polyethylene (LDPE 1) with a density of 0.925 g/cm³ and melt index of 1.0 dg/min (according to ASTM D1238, 190°C/2.16 kg) and a substantially random ethylene styrene interpolymers (ESI 1) with a nominal styrene content of 69 wt % and melt index of 1 dg/min (according to ASTM D1238, 190°C/2.16 kg) was fed to the extruder. The levels of additives used in the formulation are

reported in parts by weight per hundred parts by weight of the polymer resin blend (pph). The ESI 1 resin contained approximately 1 pph of dusted talc as an anti-block agent that acts as a powerful nucleator. Isobutane at 8.5 pph was injected into the mixing zone and glycerol monostearate at 1.5 pph was melt injected. 0.1 pph Irganox™ 1010 antioxidant (Tetrakis [methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)]) methane and 3.2 pph carbon black concentrate were fed into the extruder. The flame retardant package comprised 5.5 pph of the brominated flame retardant (PE-68, tetrabromobisphenol A bis (2,3-dibromopropyl ether) 30% concentrate in LDPE) and 0.55 pph of the synergist (TMS™ antimony trioxide, 1.5 micron average particle size, 80% concentrate in LDPE).

The gel residence time in the extrusion line was 45 min. The gel temperature was the highest in the mixing zone (197°C) and the gel pressure was highest at the gear pump outlet (17000 kPa). The hot gel was cooled to the foaming temperature (106°C). The gel temperature of the adjustable die (50 mm wide x 3 mm high) was maintained at 103.4°C and the pressure at the die was kept at 1170 kPa. Note the die pressure is approximately 2X the prefoaming critical die pressure. Macrocellular foam of excellent quality was obtained.

For the run made with the flame retardant package (Ex 5), the average cell size was 5.5 mm and the fresh density was 31.7 kg/m³. The cell size is significantly smaller than that of Example 4.

The flame retardant foam passed the UL-94 test with 94 HBF rating and the ASTM E-84 Steiner Tunnel test with Class A rating

The flame retardant foam with skin, no perforations and 25 mm thickness was tested for acoustic performance using ASTM E-1050 (Impedance Tube Method). The results are tabulated below:

Table 5

Example #	Sound absorption coefficients (SAC)					Max SAC (0-4000 Hz)		Average
	250 Hz	500 Hz	1000 Hz	2000 Hz	4000 Hz	SAC max	Frequency ¹	
Ex 5	0.1	0.2	0.175	0.2	0.35	0.35	4000	0.17

¹ Frequency corresponding to the maximum sound absorption

² Average SAC is the mean SAC of the following frequencies: 250 Hz, 500 Hz, 1000 Hz, 2000 Hz. The flame retardancy of the foam is adequate. The acoustics of the smaller cell foam is not as good as that of the larger cell foam of Example 4. Cell size clearly has a big impact on sound absorption performance. Thus, foam formulations should contain low, preferably zero, levels of nucleating agents such as talc (magnesium silicate), calcium stearate, barium stearate, etc.

Example 6

This example illustrates the effect of additives like glycerol monostearate and propylene glycol/ethanol mixtures on foam cell size and hence acoustic performance.

Trials were made using the equipment and process conditions detailed in Example 1. The levels of additives used in the formulation are reported in parts by weight per hundred parts by weight of the polymer resin blend (pph). The following formulation was used: low density polyethylene (LDPE 1) with a density of 0.925 g/cm³ and melt index of 1.0 dg/min (according to ASTM D1238, 190°C/2.16 kg), 9 pph isobutane, 5 pph of the brominated flame retardant (PE-68, tetrabromobisphenol A bis (2,3-dibromopropyl ether) 30% concentrate in LDPE) and 2 pph of the synergist (TrutintTM 50 antimony trioxide 80% concentrate in LDPE). The glycerol mono stearate (GMS) level (percent by weight based on polymer) was varied with all other conditions kept the same. The results are presented in Table 6 and show that an increase in GMS level results in an increase in cell size but that beyond a critical value, increase in GMS level results in a decrease in cell size. Note that GMS increases cell size during foaming and provides dimensional stability during aging.

Table 6

Example #	GMS level ¹ , pph	Average cell size ² , mm
Ex 6a	2.5	5.9
Ex 6b	5.0	7.3
Ex 6c	7.5	4.4

¹ parts by weight per hundred parts by weight polymer

² 3-d average cell size measured by ASTM D3576

Example 7

Trials were made using the equipment and process conditions detailed in Example 4. The following formulation was used: 70/30 wt % blend of low density polyethylene (LDPE 1) with a density of 0.925 g/cm³ and melt index of 1.0 dg/min (according to ASTM D1238,

190°C/2.16 kg) and a substantially random ethylene styrene interpolymers (ESI, i) with a nominal styrene content of 69 wt % and melt index of 1 dg/min (according to ASTM D1238, 190°C/2.16 kg), 9 pph isobutane, 0.4 pph glycerol mono stearate, 0.1 pph Irganox 1010 antioxidant (Tetrakis [methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)] methane and 1.5 pph carbon black concentrate. The level of the 75/25 polypropylene glycol/ethanol (PPG/EtOH) mixture was varied with all other conditions kept the same and the results are presented in Table 7A. The results show that an increase in the level of the polypropylene glycol/ethanol mixture over the range studied results in an increase in cell size and counteracts some of the nucleating tendencies of the flame retardancy additives.

TABLE 7A

Example #	PPG/EtOH level ¹ , pph	Average cell size ² , mm
Ex 7a	0.0	4.0
Ex 7b	1.35	5.5
Ex 7c	2.0	6.0

¹ parts by weight per hundred parts by weight polymer

² 3-d average cell size measured by ASTM D3576

The following resin formulation comprising polyethylene, polypropylene and ethylene styrene interpolymers was also used: 28/2/70 wt % blend of low density polyethylene (LDPE 1) with a density of 0.925 g/cm³ and melt index of 1.0 dg/min (according to ASTM D1238, 190°C/2.16 kg) and a substantially random ethylene styrene interpolymers (ESI 1) with a nominal styrene content of 69 wt % and melt index of 1 dg/min (according to ASTM D1238, 190°C/2.16 kg) and a polypropylene high melt strength (HMS PP 1) with a melt flow rate of 3g/10min (according to ASTM D1238, 230°C/2.16 kg).

The levels of additives used in the formulation are reported in parts by weight per hundred parts by weight of the polymer resin blend (pph). 8 pph isobutane, 0.3 pph glycerol mono stearate, 0.1 pph Irganox 1010 antioxidant (Tetrakis [methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)] methane and 1.5 pph carbon black concentrate. The flame retardant package comprising 3.8 pph tetrabromobisphenol A bis 2,3-dibromopropyl ether (PETM-68) and 1.5 pph TRUTINTTM 50 antimony trioxide. The level of the 75/25

polypropylene glycol/ethanol (PPG/EtOH) mixture was varied with all other conditions kept the same and the results are presented in Table 7B. The results show that an increase in the level of the polypropylene glycol/ethanol mixture over the range studied results in an increase in cell size and counteracts some of the nucleating tendencies of the flame retardancy additives.

TABLE 7B

Example #	PPG/EtOH level ¹ , pph	Average cell size ² , mm
Ex 7d	0.0	4.2
Ex 7e	2.0	6.5

¹ parts by weight per hundred parts by weight polymer

² 3-d average cell size measured by ASTM D3576

The foams of Ex7d and 7e made with the PE-68/ Sb₂O₃ FR package passed the DIN-4102 test with B2 rating.

Example 8

This example describes the formulation and process conditions to make large cell foam with flame retardants and synergists.

Trials were made using equipment and process conditions similar to that used in Example 4. The following resins were used: 85/15 wt %blend of low density polyethylene (LDPE 1) with a density of 0.925 g/cm³ and melt index of 1.0 dg/min (according to ASTM D1238, 190°C/2.16 kg) and a substantially random ethylene styrene interpolymmer (ESI 1) with a nominal styrene content of 69 wt % and melt index of 1 dg/min (according to ASTM D1238, 190°C/2.16 kg). The levels of additives used in the formulation are reported in parts by weight per hundred parts by weight of the polymer resin blend (pph). 0.1 pph Irganox antioxidant (Tetrakis [methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)]) methane was metered into the extruder. The flame retardants used included brominated agents (PETM-68, (tetrabromobisphenol A bis (2,3-dibromopropyl ether) 30% concentrate in LDPE; and chlorinated agents (ChlorezTM700). The inorganic synergist used was antimony trioxide (TMSTM, 80% concentrate in LDPE) and the organic synergist used was polycumyl (poly 1,4-

diisopropyl benzene). Isobutane at 8.5 pph was injected into the mixing zone and glycerol monostearate at 1.5 pph was melt injected. The first four runs used no color concentrates for a white foam but the last two runs used 3.2 pph of black concentrate for a black foam. The control foam (Comparative Ex 2) used no flame retardant or synergist.

- 5 The gel residence time in the extrusion line was 45 min. The gel temperature was the highest in the mixing zone (about 197°C) and the gel pressure was highest at the gear pump outlet (about 18200 kPa). The hot gel was cooled to the foaming temperature (105°C). The temperature of the adjustable die (50 mm wide x 3.2 mm high) was maintained at 105°C and the pressure at the die was kept at 1260 kPa. Note the die pressure is approximately 2X the
- 10 prefoaming critical die pressure.

Table 8

Example #	Flame retardant, pph ¹	Synergist, pph ¹	Die pressure, kPa	Av cell size ² , mm	Density ³ , kg/m ³
Comp Ex 2	None	None	1260	6.0	34.0
Ex 8a	PE-68, 3	Sb ₂ O ₃ , 1	1240	6.0	34.3
Ex 8b	PE-68, 5	Sb ₂ O ₃ , 1	1130	6.0	34.2
Ex 8c	Chlorez TM 700, 2.25	Sb ₂ O ₃ , 2.25	1170	4.6	30.2
Ex 8d	PE-68, 3	Sb ₂ O ₃ , 1	1220	6.4	34.0
Ex 8e	PE-68, 5.5	Sb ₂ O ₃ , 0.55	1170	5.5	31.7

¹ parts by weight per hundred parts by weight polymer

² 3-d average cell size measured by ASTM D3576

³ density measured by ASTM D3575 suffix W method B

- 15 The foam properties are presented in Table 8. All the flame retardant packages produced moderate to large cell foam of excellent quality, which indicates that the formulations have low nucleating potential. The control foam (Comp Ex 2) failed the DIN-4102 test (B2 rating). The foams of Ex 8 made with the PE-68/Sb₂O₃ FR package passed the UL-94 test with HBF rating. The foams of Ex 8 made with ChlorezTM700/Sb₂O₃ passed the ASTM E-84 test with Class A
- 20 rating.

Example 9

This example describes the formulation and process conditions to make large cell foam with a binary blend of brominated and chlorinated flame retardants and a flame retardant synergist.

- 5 Trials were made using equipment and process conditions were very similar to that used in Example 4. Low density polyethylene (LDPE 1) with a density of 0.925 g/cm³ and melt index of 1.0 dg/min (according to ASTM D1238, 190°C/2.16 kg) was used. The levels of additives used in the formulation are reported in parts by weight per hundred parts by weight of the polymer resin blend (pph). 0.1 pph Irganox antioxidant (Tetrakis
- 10 [methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)]) methane was metered into the extruder. The flame retardants used included a ternary blend of brominated agent 4.1 pph PETM-68, (tetrabromobisphenol A bis (2,3-dibromopropyl ether) 30% concentrate in LDPE with chlorinated agent 2 pph ChlorezTM700 with an inorganic synergist 2 pph antimony trioxide (TMSTM concentrate in LDPE). Isobutane at 9 pph was injected into the mixing zone
- 15 and glycerol monostearate at 0.2 pph was melt injected. The runs used 1.5 pph of black concentrate for a black foam.

- The gel residence time in the extrusion line was 45 min. The gel temperature was the highest in the mixing zone (about 197°C) and the gel pressure was highest at the gear pump outlet (about 12106 kPa). The hot gel was cooled to the foaming temperature (108°C). The
- 20 temperature of the adjustable die (50 mm wide) was maintained at 106°C.

Table 9

Example #	Flame retardant, pph ¹	Synergist, pph ¹	Av cell size ² , mm	Density ³ , kg/m ³
Ex 9	PE-68, 4.1 Chlorez TM 700, 2	Sb ₂ O ₃ , 2	6.3	33.9

¹ parts by weight per hundred parts by weight polymer

² 3-d average cell size measured by ASTM D3576

³ density measured by ASTM D3575 suffix W method B

- 25 The foam properties are presented in Table 9. This flame retardant package produced large cell foam of excellent quality, which indicates that the formulation has low nucleating

potential. The foam of Ex 9 made with the PE-68/ ChlorezTM700/Sb₂O₃ FR package passed the UL-94 test with HF-1 rating and passed the DIN-4102 test with B2 rating.

Example 10

5 This example describes the formulation and process conditions to make large cell foam using a blend of polyethylene and polypropylene with flame retardants and synergists.

Trials were made using equipment and process conditions were very similar to that used in Example 4. The following resins were used: 40/60 wt %blend of low density polyethylene (LDPE 1) with a density of 0.925 g/cm³ and melt index of 1.0 dg/min (according to ASTM D1238, 190°C/2.16 kg) and a polypropylene high melt strength (HMS PP 1) with a
10 melt flow rate of 3g/10min (according to ASTM D1238, 230°C/2.16 kg). The levels of additives used in the formulation are reported in parts by weight per hundred parts by weight of the polymer resin blend (pph). 0.1 pph Irganox antioxidant (Tetrakis [methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)] methane was metered into the extruder. The flame
15 retardants used included brominated agents (PETM-68, (tetrabromobisphenol A bis (2,3-dibromopropyl ether) 30% concentrate in LDPE; and chlorinated agents (ChlorezTM700). The inorganic synergist used was antimony trioxide (TMSTM, 80% concentrate in LDPE). Isobutane at 10 pph was injected into the mixing zone. The runs used 1.5 pph of black concentrate for a black foam. The control foam used no flame retardant or synergist.

20 The gel residence time in the extrusion line was 45 min. The gel temperature was the highest in the mixing zone (about 225°C) and the gel pressure was highest at the gear pump outlet (about 21474 kPa). The hot gel was cooled to the foaming temperature (155°C). The temperature of the adjustable die (50 mm wide) was maintained at 152°C.

Table 10

Example #	Flame retardant, pph ¹	Synergist, pph ¹	Av cell size ² , mm	Density ³ , kg/m ³
Comp	None	None	9.0	27.5
Ex 10a	PE-68, 3	Sb ₂ O ₃ , 1	6.5	31.0
Ex 10b	PE-68, 5 Chlorez TM 700, 1.5	Sb ₂ O ₃ , 1.5	3.6	28.7
Ex 10c	PE-68, 3 Chlorez TM 700, 1	Sb ₂ O ₃ , 1	3.6	28.7

¹ parts by weight per hundred parts by weight polymer

² 3-d average cell size measured by ASTM D3576

³ density measured by ASTM D3575 suffix W method B

- 5 The foam properties are presented in Table 10. All the flame retardant packages produced moderate to large cell foam of excellent quality, which indicates that the formulations have low nucleating potential. The control foam (Comp) failed the DIN-4102 test (B2 rating) and failed UL-94 test. The foams of Ex 10 made with the PE-68/Sb₂O₃ FR package passed the DIN-4102 test with B2 rating and passed UL-94 test with HF-1 rating. The foams of Ex 10
- 10 made with PE-68/ChlorezTM700/Sb₂O₃ passed the the DIN-4102 test with B2 rating and passed UL-94 test with HF-1 rating.

Example 11

- Example 11 illustrates the effect of nucleating agents on cell size. This example also
- 15 compares the foam properties obtained with flame retardant packages comprising inorganic and organic synergists.

- The formulation and process conditions were very similar to that used in the earlier section. The ESI 1 resin is typically dusted with talc to prevent blocking (agglomeration of pellets). Batch to batch variations exist in the talc level of the dusted resin. Nucleating
- 20 agents like talc (magnesium silicate), calcium stearate, barium stearate, etc., increase the number of nuclei that are created during foaming and produce small cells. The cell size

decreases as the level of nucleator increases until a critical level, beyond which no effect is observed.

The foam properties are presented in Table 11. The flame retardant package comprising 3 pph tetrabromobisphenol A bis 2,3-dibromopropyl ether (PETM-68) and 1 pph TRUTINTTM 50 antimony trioxide at the same ratio (3:1) as used in the earlier section produced small cell foam (<3mm) that is acoustically inactive. A higher level of dusted talc in the formulation is responsible for this cell size reduction. The flame retardant package comprising 3.5 pph of SAYTEXTM HP-900 hexabromocyclo-dodecane (HBCD) with 0.3 pph of poly 1,4-diisopropylbenzene (polycumyl) was added to the formulation. A foam with moderate cell size was obtained (>3 mm). Synergists with a low level of insoluble particles are preferred for making large cell acoustic foam because of their lower nucleation tendency. The flame retardant package also comprising 4.6 pph tetrabromobisphenol A bis 2,3-dibromopropyl ether (PETM-68) and 1.9 pph TRUTINTTM 50 antimony trioxide with increasing percentage of ESI.

For a fixed flame retardant composition (4.6 pph tetrabromobisphenol A bis 2,3-dibromopropyl ether (PETM-68) and 1.9 pph TRUTINTTM 50 antimony trioxide), the level of ESI (and hence, the level of talc) in the formulation was varied and the results are presented in Table 11. The results show that an increase in the level of ESI in the blend caused a reduction in the cell size due to the nucleation caused by the dusted talc. However, no negative effect on flame retardancy was observed in the range studied as all foams passed the DIN 4102 fire test with B2 rating

TABLE 11

Example #	Ratio LDPE/ESI	Flame retardant, pph ¹	Synergist, pph ¹	Average cell size ² , mm
Ex 11a	85/15	PE-68, 3	Sb ₂ O ₃ , 1	2.7
Ex 11b	85/15	SAYTEX™ HP-900, 3.5	Polycumyl, 0.3	4.0
Ex 11c	100/0	PE-68, 4.6	Sb ₂ O ₃ , 1.9	6.9
Ex 11d	95/5	PE-68, 4.6	Sb ₂ O ₃ , 1.9	4.4
Ex 11e	90/10	PE-68, 4.6	Sb ₂ O ₃ , 1.9	2.5

¹ parts by weight per hundred parts by weight polymer

² 3-d average cell size measured by ASTM D3576

The flame retardant foam passed the DIN 4102 fire test with B2 rating.

5

Example 12

This example describes the formulation and the process conditions to make large cell acoustic foam with flame retardants and synergists. The foams were prepared in commercial extrusion equipment. The large scale single screw extruder consisted of a feeding zone for solid additives and resins, a melting zone and a metering zone. In addition, there was a mixing zone with a port to inject the blowing agent and liquid additives, a cooling zone to uniformly cool the melt to the foaming temperature and a die body. A gear pump between the metering and mixing zones stabilized the melt flow rate. A static mixer in the cooling zone aided in gel temperature uniformity. The foaming temperature is the optimal gel temperature for foaming when the melt strength is high enough to stabilize the foam and prevent cell collapse. The melt is extruded through a die to room temperature and pressure to expand the gel and stabilize the resulting foam.

The levels of additives used in the formulation are reported in parts by weight per hundred parts by weight of the polymer resin blend (pph). For Comparative Example 3, low density polyethylene (LDPE 2) with a density of 0.924 g/cc and melt index of 1.8 dg/min (according to ASTM D1238, 190°C/2.16 kg) was fed along with 0.3 pph Irganox antioxidant (Tetrakis [methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)]) methane and 1.5 pph of black concentrate (2.5% carbon black) in the same LDPE resin. Isobutane at 8.5

pph was injected into the mixing zone and glycerol monostearate at 1.5 pph was melt injected. For the flame retardant run, the compounded FR package was dosed at 3.5 pph Chlorez™ 760 and 3.5 pph antimony trioxide.

5 The gel residence time in the extrusion line was 45 min. The gel temperature was the highest in the mixing zone (192°C) and the gel pressure was highest at the gear pump outlet (8800 kPa). The hot gel was cooled to the foaming temperature (112.5°C). The temperature of the fixed, variable cross-section die was maintained at 112.5°C. The die body was not equipped with a pressure transducer for determining the die pressure.

10 Knowing the die geometry's, the die pressure in the large scale extruder can be estimated from the die pressure in the pilot scale extruder by the following procedure. The procedure assumes that the viscosity of the polymer melt, the gel foaming temperature and the formulation are the same for both lines.

The shear rates for the non-Newtonian fluid (γ°) in the two lines are therefore the same and given by the Rabinowitsch equation:

15
$$\gamma^\circ = \{(2n+1)/3n\} * 6Q/(w*h*h)$$

where n is the power law index ($\tau = \gamma^\circ n$), Q is the flow rate and w and h are the width and height of the die.

For the pilot line, the flow rate was 60 kg/hr = 132 lb/hr. The die pressure was determined at two die slit settings.

20 When the slit die dimensions were 50 mm width (1.97") and 3.3 mm (0.13") height, the die pressure was 1390 kPa (2X prefoaming critical die pressure) and shear rate calculated from the above equation (for n=1) is 215 sec⁻¹

25 When the slit die dimensions were 50 mm width (1.97") and 0.85 mm (0.13") height, the die pressure was 3130 kPa (4.5X prefoaming critical die pressure) and shear rate calculated from the above equation (for n=1) is 3341 sec⁻¹

For the large line, the flow rate was 1180 kg/hr = 2600 lb/hr. The cross-section of the die is non-uniform and a representative gap needs to be determined. This was done by dividing the die into sections from the center of the die to the ends and by calculating the incremental

and cumulative areas for each section. The cumulative area was then plotted against the section distance from the center of the die, resulting in a very non-linear curve. Different average gaps were assumed and the cumulative area was then plotted against the section distance from the centerline resulting in a linear curve with different slopes. The best fit line was obtained with the average gap which corresponded to the cumulative area of the section at 2/3 the full width divided by the section distance from the center of the die. For the large die, the average gap as calculated as 3.22 mm and the effective width of the die was 332mm. The shear rate calculated from the above equation was 670 sec^{-1} . The die pressure of the large line was estimated at 2.4X the prefoaming critical die pressure.

For Comparative Example 3 made with no flame retardant package, the cell size was 7 mm and the fresh density was 30.4 kg/m^3 . For Example 11 made with the flame retardant package, the cell size was 4 mm (horizontal) x 12 mm (vertical) and the fresh density was 30.4 kg/m^3 .

The foam of Comparative Example 3 failed the DIN-4102 fire test and the UL-94 fire test. The flame retardant foam of Example 12 passed the DIN-4102 fire test with B2 fire rating and passed the UL-94 fire test with HF1 rating. The foams of Example 12 and Comparative Example 3 both with no skin, no perforations and 35 mm thickness were tested for acoustic performance using ASTM E-1050 (Impedance Tube Method). The acoustic results are comparable as summarized in Table 12:

Table 12

Example #	Sound absorption coefficients (SAC)					Max SAC (0-4000 Hz)		Average
	250 Hz	500 Hz	1000 Hz	2000 Hz	4000 Hz	SAC max	Frequency ¹	
Comp Ex 3	0.09	0.52	0.56	0.54	0.46	0.76	630	0.43
Ex 12	0.11	0.52	0.41	0.45	0.5	0.63	630	0.37

¹ Frequency corresponding to the maximum sound absorption

² Average SAC is the mean SAC of the following frequencies: 250 Hz, 500 Hz, 1000 Hz, 2000 Hz,

Example 13.

This example describes the formulation and the process conditions to make large cell acoustic foam made with a different flame retardant/synergist package.

Runs were made in commercial extrusion equipment on a different large line. For the flame retardant foam run, a 97/3 blend of low density polyethylene (LDPE 2) with a density of 0.924 g/cm^3 and melt index of 1.8 dg/min (according to ASTM D1238, $190^\circ\text{C}/2.16 \text{ kg}$) and ethylene styrene interpolymers (ESI 1) with a nominal styrene content of 69% and melt index of 1 dg/min (according to ASTM D1238, $190^\circ\text{C}/2.16 \text{ kg}$) was fed. 0.5 pph Irganox antioxidant (Tetrakis [methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)]) methane and 2 pph of black concentrate (25% carbon black in LDPE 2) were also fed to the extruder. Isobutane at 9 pph was injected into the mixing zone and glycerol mono stearate at 0.75 pph was melt injected. The first flame retardant formulation (FR1) comprised 5 pph of PE-68 (tetrabromobisphenol A bis (2,3-dibromopropyl ether) 30% concentrate in LDPE) and 1.5 pph of antimony trioxide (TrutintTM 50, 3 micron particle size, 80% concentrate in LDPE). The second flame retardant formulation (FR2) comprised 4 pph of PE-68 (tetrabromobisphenol A bis (2,3-dibromopropyl ether) 30% concentrate in LDPE) and 2 pph of antimony trioxide (TrutintTM 50, 80% concentrate in LDPE).

The gel residence time in the extrusion line was 45 min. The gel temperature was the highest in the mixing zone (190°C). The hot gel was cooled to the foaming temperature (112.5°C). The temperature of the fixed, variable cross-section die was maintained at 112.5°C . The die body was not equipped with a pressure transducer for determining the die pressure.

For the large line, the flow rate was $680 \text{ kg/hr} = 1500 \text{ lb/hr}$. For the large die, the average gap was calculated as 3.22mm and the effective width of the die was 332mm. The shear rate was obtained as 386 sec^{-1} when calculated using the procedure detailed in the earlier section. The die pressure of the large line was estimated at 2.1X the prefoaming critical die pressure.

Large cell foam with cell size of 6 mm (horizontal) x 6 mm (extrusion) x 8 mm (vertical) was obtained. The first flame retardant formulation passed the UL-94 fire test with HBF rating and passed the DIN-4102 fire test with B2 fire rating. The second flame retardant formulation

passed only the UL-94 fire test with HBF rating. The flame retardant foams were tested using ASTM E-1050 (Impedance Tube Method). The foams were tested without skins, unperforated and 35 mm in thickness. The acoustic results are summarized in Table 13.

Table 13.

Example #	Flame Retardant Package	Sound absorption coefficients (SAC)					Max SAC (0-4000 Hz)		Average
		250 Hz	500 Hz	1000 Hz	2000 Hz	4000 Hz	SAC max	Frequency ¹	
Ex 13a	FR1	0.076	0.311	0.933	0.657	0.768	0.933	1000	0.49
Ex 13b	FR2	0.070	0.247	0.924	0.662	0.789	0.924	1000	0.48

¹ Frequency corresponding to the maximum sound absorption

² Average SAC is the mean SAC of the following frequencies: 250 Hz, 500 Hz, 1000 Hz, 2000 Hz,

CLAIMS

1. A process for preparing a macrocellular acoustic foam from a polymeric resin composition, said process comprising subjecting a foamable gel comprising at least one blowing agent and at least one polymeric resin composition to an extrusion process, wherein said polymeric resin composition comprises
 - A) one or more homopolymers of ethylene, one or more C₃-C₂₀ α -olefin polymer, or a combination thereof;
 - B) one or more halogenated flame retardants;
 - C) optionally, one or more polymers other than that of Component A; and
 - D) optionally, one or more flame retardant synergists,characterized by conducting the extrusion process at a die pressure greater than the prefoaming critical die pressure but less than or equal to four times that of said prefoaming critical die pressure.
2. The process of Claim 1; wherein
 - A) Component A is one or more homopolymers of ethylene, or one or more C₃-C₁₀ α -olefin polymers, or a combination thereof;
 - B) said halogenated flame retardant, Component B comprises one or more of hexahalodiphenyl ethers, octahalodiphenyl ethers, decahalodiphenyl ethers, decahalobiphenyl ethanes, 1,2-bis(trihalophenoxy) ethanes, 1,2-bis(pentahalophenoxy) ethanes, hexahalocyclododecane, a tetrahalobisphenol-A, ethylene(N, N')-bis-tetrahalophthalimides, tetrabromobisphenol A bis (2,3-dibromopropyl ether) tetrahalophthalic anhydrides, hexahalobenzenes, halogenated indanes, halogenated phosphate esters, halogenated paraffins, halogenated polystyrenes, polymers of halogenated bisphenol-A and epichlorohydrin, or a combination thereof;
 - C) Component C when present comprises one or more of; a substantially random interpolmer, a heterogeneous ethylene/ α -olefin interpolmer, a homogeneous

ethylene/ α -olefin interpolymers, a thermoplastic olefin, a styrenic block copolymer, a styrenic homopolymer or copolymer, an elastomer, a thermoplastic polymer, a thermoset polymer; a vinyl or vinylidene halide homopolymer or copolymer, an engineering thermoplastic, or a combination thereof; and

- D) Component D when present comprises one or more metal oxides, boron compounds, and organic peroxides, or a combination thereof.

3. The process of Claim 1; wherein

- A) Component A is one or more homopolymers of ethylene, or one or more propylene polymers, or a combination thereof;
- B) said halogenated flame retardant, Component B, comprises hexabromocyclododecane (HBCD), tetrabromobisphenol A bis (2,3-dibromopropyl ether), PETM-68, or a combination thereof;
- C) Component C when present comprises one or more of; a substantially random interpolymers, a heterogeneous ethylene/ α -olefin interpolymers, a homogeneous ethylene/ α -olefin interpolymers, or a combination thereof; and
- D) said flame retardant synergist, Component D when present, comprises one or more of; iron oxide, tin oxide, zinc oxide, aluminum trioxide, alumina, antimony trioxide, antimony pentoxide, bismuth oxide, molybdenum trioxide, tungsten trioxide, zinc borate, antimony silicates, zinc stannate, zinc hydroxystannate, ferrocene, dicumyl peroxide, and polycumyl peroxide, or a combination thereof.

4. The process of Claim 3; wherein

- A) Component A is LDPE, polypropylene, or a combination thereof;
- B) Component B is hexabromocyclododecane (HBCD), tetrabromobisphenol A bis (2,3-dibromopropyl ether), PETM-68, or a combination thereof;

- C) Component C when present is a substantially random ethylene/styrene interpolymer, a substantially linear ethylene/1-octene copolymer; or a combination thereof; and
 - D) Component D when present is antimony trioxide.
5. The process of any one of the preceding claims in which the die pressure is less than or equal to three times that of said prefoaming critical die pressure.
6. The process of any one of the preceding claims in which the die pressure is less than or equal to two times that of said prefoaming critical die pressure.
7. A macrocellular acoustic foam comprising;
- E) one or more homopolymers of ethylene, one or more C₃-C₂₀ α -olefin polymers, or a combination thereof;
 - F) one or more halogenated flame retardants;
 - G) optionally, one or more polymers other than that of Component A; and
 - H) optionally, one or more flame retardant synergists.
8. The macrocellular acoustic foam of Claim 7; wherein
- A) Component A is one or more homopolymers of ethylene, or one or more C₃-C₁₀ α -olefin polymers, or a combination thereof;
 - B) said halogenated flame retardant, Component B comprises one or more of hexahalodiphenyl ethers, octahalodiphenyl ethers, decahalodiphenyl ethers, decahalobiphenyl ethanes, 1,2-bis(trihalophenoxy) ethanes, 1,2-bis(pentahalophenoxy) ethanes, hexahalocyclododecane, a tetrahalobisphenol-A, ethylene(N, N')-bis-tetrahalophthalimides, tetrabromobisphenol A bis (2,3-dibromopropyl ether), tetrahalophthalic anhydrides, hexahalobenzenes,

halogenated indanes, halogenated phosphate esters, halogenated paraffins, halogenated polystyrenes, polymers of halogenated bisphenol-A and epichlorohydrin, or a combination thereof;

- C) Component C when present comprises one or more of; a substantially random interpolymer, a heterogeneous ethylene/ α -olefin interpolymer, a homogeneous ethylene/ α -olefin interpolymer, a thermoplastic olefin, a styrenic block copolymer, a styrenic homopolymer or copolymer, an elastomer, a thermoplastic polymer, a thermoset polymer; a vinyl or vinylidene halide homopolymer or copolymer, an engineering thermoplastics, or a combination thereof; and
- D) Component D when present comprises one or more metal oxides, boron compounds, and organic peroxides, or a combination thereof.

9. The macrocellular acoustic foam of Claim 7; wherein

- A) Component A is a homopolymer of ethylene, or a propylene polymer, or a combination thereof;
- B) said halogenated flame retardant, Component B comprises hexabromocyclododecane (HBCD), tetrabromobisphenol A bis (2,3-dibromopropyl ether), PETM-68, or a combination thereof;
- C) Component C when present comprises a substantially random interpolymer, a heterogeneous ethylene/ α -olefin interpolymer, a homogeneous ethylene/ α -olefin interpolymer, or a combination thereof; and
- D) said flame retardant synergist, Component D when present, comprises one or more iron oxide, tin oxide, zinc oxide, aluminum trioxide, alumina, antimony trioxide, antimony pentoxide, bismuth oxide, molybdenum trioxide, and tungsten trioxide, zinc borate, antimony silicates, zinc stannate, zinc hydroxystannate, ferrocene, dicumyl peroxide, and polycumyl peroxide, or a combination thereof.

10. The macrocellular acoustic foam of Claim 9; wherein
- A) Component A is LDPE or polypropylene, or a combination thereof;
 - B) Component B is hexabromocyclododecane (HBCD), tetrabromobisphenol A bis (2,3-dibromopropyl ether), PETM-68, or a combination thereof;
 - C) Component C when present is a substantially random ethylene/styrene interpolymers, a substantially linear ethylene/1-octene copolymer; or a combination thereof; and
 - D) Component D when present is antimony trioxide.
11. A macrocellular acoustic foam obtainable by the process according to any one of claims 1 to 6.
12. The macrocellular acoustic foam of any one of claims 7 to 11 having an average cell size according to ASTM D3576 in the range from 3 mm to 10 mm.
13. The macrocellular acoustic foam of Claims 7 - 11, in the form of an office partition, automotive decoupler, domestic appliance sound insulation, sound proofing panel or machine enclosure.
14. Use of the macrocellular foam of any one of claims 7 to 12 as an acoustic absorption material.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
27 September 2001 (27.09.2001)

PCT

(10) International Publication Number
WO 01/70859 A3

- (51) International Patent Classification⁷: C08J 9/00 // C08L 23/02
Titeluls. F-67410 Drusenheim (FR). PARK, Chung, P. [US/DE]; Schulstrasse 10a, 76532 Baden-Baden (DE).
- (21) International Application Number: PCT/US01/04594 (74) Agent: HOWARD, Dan, R.; The Dow Chemical Company, Intellectual Property, P.O. Box 1967, Midland, MI 48641-1967 (US).
- (22) International Filing Date: 13 February 2001 (13.02.2001)
- (25) Filing Language: English (81) Designated States (national): AU, BR, CA, CN, CZ, HU, IL, IN, JP, KR, MX, NO, RU, US, ZA.
- (26) Publication Language: English (84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).
- (30) Priority Data:
60/190,717 17 March 2000 (17.03.2000) US
- (71) Applicant (for all designated States except US): THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Midland, MI 48674 (US).
- Published:
— with international search report
- (88) Date of publication of the international search report:
24 January 2002
- (72) Inventors; and
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WO 01/70859 A3

(54) Title: PREPARATION OF A MACROCELLULAR ACOUSTIC FOAM

(57) Abstract: A process for making a macrocellular acoustic foam is disclosed in which a foamable gel comprising a blowing agent and a polymeric resin composition is subjected to an extrusion process characterized by a die pressure greater than the prefoaming critical die pressure but less than or equal to four times that of said prefoaming critical die pressure and macrocellular foams are disclosed obtainable by that process which are made of: A) one or more homopolymers of ethylene, one or more C₃-C₂₀ α -olefin polymers, or a combination thereof; B) one or more halogenated flame retardants; C) optionally, one or more polymers other than that of Component A; and D) optionally, one or more flame retardant synergists.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 01/04594

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08J9/00 //C08L23/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 188 295 A (DONALD E. BALLAST) 8 June 1965 (1965-06-08) column 4, line 62-74 example 8 claims 2,7,8,11	1,2,7,8, 11-14
A	WO 92 19439 A (DOW CHEMICAL CO) 12 November 1992 (1992-11-12) example 1; table 1 claims	1-14



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

31 August 2001

Date of mailing of the international search report

14/09/2001

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FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-14 partly

Present claims 1-14 relate to a process defined (inter alia) by reference to the following parameter:

P1: the prefoaming critical die pressure.

The use of this parameter in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT.

It is impossible to compare the parameter the applicant has chosen to employ with what is set out in the prior art.

The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to the parts relating to the method mentioned in the description at pages 33-45.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

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INTERNATIONAL SEARCH REPORT

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